INVESTIGATING THE SOURCES AND FATE OF MONOMETHYLMERCURY AND DIMETHYLMERCURY IN THE ARCTIC MARINE BOUNDARY LAYER AND WATERS

A Dissertation Submitted to the Committee on Graduate Studies in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy in the Faculty of Arts and Science

TRENT UNIVERSITY
Peterborough, Ontario, Canada

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Environmental and Life Sciences Ph.D. Program
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ABSTRACT

Investigating the sources and fate of monomethylmercury and dimethylmercury in the arctic marine boundary layer and open waters

Pascale Anabelle Baya

Monomethylmercury (MMHg), the most bioavailable form of mercury (Hg) and a potent neurotoxin, is present at elevated concentrations in Arctic marine mammals posing serious health threats to the local populations relying on marine food for their subsistence living. The sources of MMHg in the Arctic Ocean surface water and the role of dimethylmercury (DMHg) as a source of MMHg remain unclear. The objective of this research was to determine the sources and fate of methylated Hg species (MMHg and DMHg) in the marine ecosystem by investigating processes controlling the presence of methylated Hg species in the Arctic Ocean marine boundary layer (MBL) and surface waters. A method based on solid phase adsorption on Bond Elut ENV was developed and successfully used for unprecedented measurement of methylated Hg species in the MBL in Hudson Bay (HB) and the Canadian Arctic Archipelago (CAA). MMHg and DMHg concentrations averaged 2.9 ± 3.6 (mean ± SD) and 3.8 ± 3.1 pg m\(^{-3}\), respectively, and varied significantly among sampling sites. MMHg in the MBL is suspected to be the product of marine DMHg degradation in the atmosphere. MMHg summer (June to September) atmospheric wet deposition rates were estimated to be 188 ± 117.5 ng m\(^{-2}\) and 37 ± 21.7 ng m\(^{-2}\) for HB and CAA, respectively, sustaining MMHg concentrations available for bio-magnification in the pelagic food web. The production and loss of methylated Hg species in surface waters was assessed using enriched stable isotope tracers. MMHg production in surface water was
observed from methylation of inorganic Hg (Hg(II)) and, for the first time, from DMHg demethylation with experimentally derived rate constants of $0.92 \pm 0.82 \times 10^{-3} \text{ d}^{-1}$ and $0.04 \pm 0.02 \text{ d}^{-1}$ respectively. DMHg demethylation rate constant ($0.98 \pm 0.51 \text{ d}^{-1}$) was higher than that of MMHg ($0.35 \pm 0.25 \text{ d}^{-1}$). Furthermore, relationships with environmental parameters suggest that methylated Hg species transformations in surface water are mainly biologically driven. We propose that in addition to Hg(II) methylation, the main processes controlling MMHg production in the Arctic Ocean surface waters are DMHg demethylation and deposition of atmospheric MMHg. These results are valuable for a better understanding of the cycle of methylated Hg in the Arctic marine environment.

Keywords: Arctic Ocean, Atmosphere, monomethylmercury, dimethylmercury, methylation and demethylation
PREFACE

The research presented in this thesis was conducted under the supervision of Professor Holger Hintelmann and consisted of laboratory work as well as sampling campaigns part of ArcticNet expeditions in the Canadian Arctic and sub-Arctic on board the Canadian Coast Guard ship (CCGS) Amundsen. While I designed, prepared and conducted the field sampling and most of the mercury related analyses, like most scientific studies, the research included in this thesis required to some extent the collaboration of other researchers who contributed their intellectual and technical expertise. I have given credit by way of authorship to people who provided supporting data, performed the analyses and made significant contributions to the manuscripts that have or will be published from this thesis (See list of publications).


Chapter 4: Baya, P. A. and Hintelmann H., Methylation and demethylation of mercury in polar marine waters. To be submitted for publication in a suitable peer reviewed journal.
If I have seen further it is by standing on the shoulders of giants.

Sir Isaac Newton

Qui n'éprouve pas de joie quand il apprend ne doit pas être enseigné.

Se passionner pour ce qui est autre, aimer, apprendre, c'est le même.

(Pascal Quignard, Vie secrète, 1998)
ACKNOWLEDGEMENTS

I am deeply grateful to Professor Holger Hintelmann, my supervisor, for his supportive, patient and very insightful guidance during my research. I went through a very steep learning curve during the past years and this is greatly due to Professor Hintelmann’s supervision and trust, which allowed me to work independently and seek his advice whenever required.

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I would like to acknowledge the financial support from Trent University Graduate Studies department for the Dean Scholarship as well funding from ArcticNet for the research project.

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I would like to thank the CCGS Amundsen crew for their dedication and genuine interest in the scientific work conducted during the expeditions. I also extend my gratitude to the
ArcticNet team for the logistic support and help, essential for the success of the sampling expeditions conducted. To the “Amundsen” family, to those who shared this unique experience in the magnificent Arctic, thank you for all the precious memories. I am deeply thankful for all the friends I’ve made; our sun lit days and nights, the long sampling hours at any time of day or night, the Sunday diners and evenings, the movie nights and of course our bar nights are all very dear memories.

A special thanks to Professor Connie Lovejoy (Laval University) for having me as a “friend” of her laboratory and her support during the writing of my thesis. Aux filles du labo Lovejoy, merci de m’avoir accueilli en tant que membre à part entière du labo des microbiologistes. Une pensée spéciale pour Sophie; celle qui fut à l’origine de cette “collaboration” et aussi pour les heures de boulot et les kilomètres de courses (bien nécessaire pour le morale) ensembles. Un grand merci à Cindy et Mary pour les petits mots d’encouragement.

I have a special thought to my family in Mauritius, for the faith they have in me and all my endeavors in life. A special thought to my big sister Syndy for her generosity and precious support and help in numerous matters. To my niece Angela for whom I had the responsibility to do nothing less but my very best, her genuine interest for my work gave me wings.

I am deeply grateful to Mathieu Ardyna for being a wonderful partner, his support and belief in me kept me going in moments of doubts, his critical reviews challenged me to thorough my thinking and analysis, his passion for scientific research is a true inspiration.
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<th>Abbreviation</th>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BE</td>
<td>Bond elut ENV</td>
<td></td>
</tr>
<tr>
<td>BT</td>
<td>Breakthrough</td>
<td></td>
</tr>
<tr>
<td>CAA</td>
<td>Canadian Arctic Archipelago</td>
<td></td>
</tr>
<tr>
<td>CB</td>
<td>Carbo trap B</td>
<td></td>
</tr>
<tr>
<td>Chl a</td>
<td>Chlorophyll a</td>
<td></td>
</tr>
<tr>
<td>DMHg</td>
<td>Dimethylmercury</td>
<td></td>
</tr>
<tr>
<td>DOC</td>
<td>Dissolved organic carbon</td>
<td></td>
</tr>
<tr>
<td>GC-ICP-MS</td>
<td>Gas chromatography inductively coupled plasma mass spectrometry</td>
<td></td>
</tr>
<tr>
<td>GEM</td>
<td>Gaseous elemental mercury</td>
<td></td>
</tr>
<tr>
<td>HB</td>
<td>Hudson Bay</td>
<td></td>
</tr>
<tr>
<td>Hg</td>
<td>Mercury</td>
<td></td>
</tr>
<tr>
<td>Hg (0)</td>
<td>Elemental mercury</td>
<td></td>
</tr>
<tr>
<td>Hg (II)</td>
<td>Inorganic reactive Hg</td>
<td></td>
</tr>
<tr>
<td>$k_m$</td>
<td>Methylation rate constant</td>
<td></td>
</tr>
<tr>
<td>$k_d$</td>
<td>Demethylation rate constant</td>
<td></td>
</tr>
<tr>
<td>MMHg</td>
<td>Monomethylmercury</td>
<td></td>
</tr>
<tr>
<td>ng</td>
<td>nanogram</td>
<td></td>
</tr>
<tr>
<td>PAR</td>
<td>Photosynthetically active radiation</td>
<td></td>
</tr>
<tr>
<td>pg</td>
<td>picogram</td>
<td></td>
</tr>
<tr>
<td>PHg</td>
<td>Particulate Hg</td>
<td></td>
</tr>
<tr>
<td>PP</td>
<td>Primary productivity</td>
<td></td>
</tr>
<tr>
<td>RGM</td>
<td>Reactive gaseous mercury</td>
<td></td>
</tr>
<tr>
<td>SCM</td>
<td>Subsurface chlorophyll maximum</td>
<td></td>
</tr>
<tr>
<td>TA</td>
<td>Tenax</td>
<td></td>
</tr>
</tbody>
</table>
List of publications

This thesis is based on the following articles:


II Baya, P. A.; Gosselin, M., Lehnherr I., St.Louis, V. L. and Hintelmann H. (2014) Determination of monomethylmercury and dimethylmercury in the Arctic marine atmosphere. Manuscript to be submitted to *Environmental Science and Technology* (Accepted September 2014)

CHAPTER 1: GENERAL INTRODUCTION

Mercury (Hg) is ubiquitous in the environment and has been widely used since ancient times due to its unique chemical and physical properties. In nature, Hg exists in its mineral form as cinnabar (mercuric sulfide, HgS) which forms a bright red pigment (vermilion) when powdered. Earliest records of Hg utilization goes back to centuries BC when cinnabar was extracted by the Incas for the production of vermilion in the Peruvian Andes in 1400 BC [1] and used by the Chinese in red ink and pigments before 1000 BC [2]. Large scale mining of Hg began prior to Roman times in Spain (Almaden) [3] and amplified during the Colonial era (1532–1900 AD) in South America with the invention of Hg amalgamation for precious metal extraction such as gold and silver [1]. Since then, mining of Hg continued and numerous applications were found for Hg such as in felt hat making, medicinal uses for treating infections and as an antiseptic, and the manufacture of chlorine and caustic soda in chloro-alkali plants. In early twentieth century, organomercurials, were introduced and they proved to be potent fungicides and were widely used in paper and paint industries and in agriculture to treat seed grain. Nowadays, Hg is still in use in artisanal gold mining and in a wide range of products including batteries, paints, switches, electronic devices, fluorescent and energy saving lamps, dental amalgam, vaccines and even cosmetics [4]. The role of mercury in technological progress is undeniable but this extensive use and release of Hg in the environment was not without disastrous human and ecological consequences. It is the same useful chemical and physical properties that make Hg one of the most important and studied contaminant in the world nowadays.
Major physical and chemical properties of mercury

Hg is the only metal which is liquid at room temperature but also exist as a gas due to its high vapour pressure. Hg has an atomic number of 80, an atomic mass of 200.59, a melting point of -39.8°C, and a boiling point of 357.3°C. Hg is found among the transition elements of the Periodic Table (d-block) and has seven stable isotopes with variable abundances (\(^{204}\text{Hg}, 6.8\%, \ 202\text{Hg}, 29.8\%, \ 201\text{Hg}, 16.7\%, \ 200\text{Hg}, 23.2\%, \ 199\text{Hg}, 16.7\%, \ 198\text{Hg}, 10.0\% \text{and} \ 196\text{Hg},0.15\%). Hg is relatively inert but readily combines with noble and other metals (e.g. Au, Ag) to form alloys (amalgams). Other unique physico-chemical properties of Hg include high surface tension, high specific gravity, low electrical resistance and constant volume expansion over a wide temperature range (-39 °C to 357 °C). Selected physical and chemical properties of some environmentally relevant Hg species are summarized in Table 1-1.

Hg speciation

Hg species show significant chemical and physical differences which determine their fate, mobility and toxicity in the environment. Cinnabar (HgS), the principal ore of Hg, forms stable bonds with reduced sulphur compounds namely thiols and sulfides and has very low solubility. Hg exists in 3 oxidation sates; 0 (Hg(0)), +1 (Hg(I) or Hg+) and +2 (Hg(II) or Hg2+). Depending on the oxidation states and binding groups, Hg species can be classified into three main groups namely elemental, inorganic and organic. In its pure elemental form, Hg(0) exists both in the liquid and gaseous state. Oxidized Hg(I), also called mercurous Hg, exist when the Hg atom has lost one electron. Hg(I) has low solubility and no known environmental significance. Hg(II), also called mercuric Hg, has two electrons lost from the Hg atom and is the most common oxidized form of Hg. Hg(II) is a relatively reactive
species in the environment and forms inorganic or organic Hg compounds depending on its binding environment.
Table 1-1. Physical and chemical properties of selected mercury compounds; compiled from [5, 6]

<table>
<thead>
<tr>
<th>Element</th>
<th>Elemental mercury</th>
<th>Mercuric chloride</th>
<th>Cinnabar</th>
<th>Methylmercury chloride</th>
<th>Dimethylmercury</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point (°C)</td>
<td>Hg(0)</td>
<td>Hg(Cl)₂</td>
<td>HgS</td>
<td>CH₃HgCl</td>
<td>(CH₃)₂Hg</td>
</tr>
<tr>
<td>-39</td>
<td>277</td>
<td>584</td>
<td>167 (Sublimation)</td>
<td>na</td>
<td></td>
</tr>
<tr>
<td>Boiling point (°C) *</td>
<td>357</td>
<td>303</td>
<td>-</td>
<td>-</td>
<td>96</td>
</tr>
<tr>
<td>Vapour Pressure (Pa)</td>
<td>0.18 §</td>
<td>8.99 x 10⁻³ §</td>
<td>negligible</td>
<td>1.76 †</td>
<td>8.30 x 10³ †</td>
</tr>
<tr>
<td>Water solubility (g L⁻¹)</td>
<td>49.4 x 10⁻⁶ §</td>
<td>66 §</td>
<td>~ 2 x 10⁻²⁴ †</td>
<td>~ 5-6 †</td>
<td>2.95 †</td>
</tr>
<tr>
<td>Henry's law coefficient</td>
<td>0.32 †</td>
<td>3.69 x 10⁻⁵ †</td>
<td>na</td>
<td>1.6 x 10⁻⁵ ‡</td>
<td>0.31 †</td>
</tr>
<tr>
<td>Octanol-water coefficient</td>
<td>4.2</td>
<td>0.1-3.3</td>
<td>na</td>
<td>1.7-2.5</td>
<td>180</td>
</tr>
</tbody>
</table>

*At 1 atmosphere
†At 25°C
§At 20°C
‡At 15°C
na - not available.
**Elemental Hg**

In its zero oxidation state, elemental Hg(0) in liquid form is silvery and referred to as metallic Hg. Hg(0) is usually referred as gaseous elemental mercury (GEM) when present in its vapor form in the atmosphere. Hg(0) in aquatic environments, in aqueous form, is referred as dissolved gaseous mercury (DGM).

**Inorganic Hg**

Inorganic Hg compounds are formed from the complexation of Hg(II) with inorganic (e.g., OH\(^-\) and Cl\(^-\)) and organic ligands, especially those containing thiol functional groups (e.g., humic and fulvic acids) [7]. The main inorganic Hg compounds include mercuric sulphide (HgS), mercuric oxide (HgO), mercuric chloride (HgCl\(_2\)) and mercuric hydroxide (Hg(OH)\(_2\)). Inorganic Hg species are chemically reactive and very soluble in water. Hg(II) has extremely high affinity for sulfhydryl groups of amino acids such as cysteine and methionine in enzymes explaining its high toxicity. Some mercury salts (e.g., HgCl\(_2\), HgBr\(_2\)) are volatile enough to exist in the gaseous form in the atmosphere, referred to as reactive gaseous mercury (RGM) [8, 9]. RGM is operationally defined as the fraction of gaseous water soluble Hg(II) that can be measured using the denuder method which involves “complexation” by reaction on potassium chloride (KCl) coated quartz annular denuders, followed by thermal desorption and quantification as Hg(0) [10]. Both Hg(0) and Hg(II) can bind or be adsorbed to particles and aerosols in the atmosphere to form particulate mercury (PHg). PHg is operationally defined as mercury on particles <2.5 µm measured by trapping on glass filters and quantification as Hg(0) following thermodesorption.
**Organic Hg species**

Organic Hg are compounds with the Hg atom covalently bonded to at least one carbon atom [5], mainly ethyl, phenyl or methyl groups. Methylated Hg compounds are the most common organic Hg compounds and are present in form of monomethylmercury (MMHg) and dimethylmercury (DMHg) in natural environments. The formation of both species by methylation, as well as their destruction, by demethylation, is believed to be both biotic [11-13] and abiotic [14]. Methylated Hg species are chemically stable but are easily degraded photo-chemically by the cleavage of the Hg-C bond in the presence of UV and visible light [5].

MMHg comprises all species containing the methylmercury cation (CH$_3$Hg$^+$) where one methyl group is bonded to the Hg atom. MMHg is very stable and binds with other ligands (e.g Cl, Br, I, OH) to form complexes. MMHg also has a high affinity for sulfur containing ligands (thiols) and in aquatic systems, MMHg forms complexes with reduced sulphur in dissolved organic matter (DOM) or cysteine groups in biota explaining its efficient transfer along the food chain and its toxicity. MMHg halides (e.g. CH$_3$HgCl) are lipid-soluble and pass easily across biological membranes [15].

DMHg, having two methyl groups bonded to the central Hg atom, is a colourless liquid with higher vapor pressure than elemental Hg (Table 1-1) and is thus very volatile. Unlike MMHg, DMHg has low solubility in water and is always hydrophobic [5]. These physical properties make DMHg a notoriously dangerous chemical. A few drops (~ 400 mg) of DMHg in contact with the skin can result in devastating neurological damage and sudden death [16, 17]. DMHg is not very stable in the atmosphere as it is oxidized by oxidants such as chlorine atom (Cl) [18], hydroxyl (OH) [19] and nitrate (NO$_3$) [20] radicals. In aqueous
environments, DMHg is believed to be unstable at low pH decomposing rapidly to MMHg [21, 22].

**Mercury measurement methods**

During the past decades, mercury research has witnessed and benefited from various technological and analytical advances. The major species of Hg have been identified and measured at concentrations as low as those found in natural water and the atmosphere improving our understanding of mercury chemistry and biochemistry in natural systems. Recent technological developments have allowed measurements with high temporal resolution of atmospheric Hg concentrations and fluxes. Techniques have been developed and tested now allowing the routine measurement of major Hg species, namely GEM, RGM and PHg in the atmosphere [8, 10, 23, 24]. The most common method for the measurement of these species involves the use of automated sampling, and amalgamation of Hg(0) on gold traps and detection by Cold Vapour Atomic Fluorescence Spectrometry (CVAFS) [25]. RGM and PHg measurements involve preliminary trapping on KCl coated annular denuder and glass or quartz fibre filter, respectively, followed by thermodesorption to release Hg(0) for detection. RGM can also be measured using mist chambers and denuders followed by chemical reduction to Hg(0) using tin chloride (SnCl₂) [8]. GEM measurements have very low sampling resolution (5 minutes) while measurements of RGM and HgP, which are present a lower concentrations in the atmosphere, require longer (a few hours) sampling for detection. These measurements have allowed for a better understanding of the spatial distribution and the short and long term variability and fate of Hg in the troposphere [26]. Significant work has also been done to identify the main factors controlling the emissions and deposition of mercury [27-29]. However, there are very few
studies on methylated Hg species in the atmosphere due to the analytical challenges of measuring suspected low concentrations and the lack of reliable and proven methods for routine measurements. A method has been developed and validated for DMHg measurement based on the trapping of DMHg on carbotrap and analysis by thermodesorption, gas chromatography (GC) separation and cold vapour atomic fluorescence spectrometry (CVAFS) [30]. The very few attempts to collect gaseous MMHg include trapping of MMHg from air into water [31], and the use of a refluxing mist chamber to trap MMHg from air in water [32]. A method based on online ethylation and specific isotope dilution was recently developed and successfully tested in the laboratory but measurements of ambient air have not been made [33].

Progress has also been made for the sampling and the measurement of Hg species in aquatic environments, which allowed for a better understanding of the geochemistry of Hg. Improved accuracy and reliability of data for low levels of Hg in various matrices has been achieved with contamination-free sampling techniques, use of appropriate material for sample storage and analysis and more reliable extraction and analytical methods [34, 35]. Today, methods exist for reliable and precise measurement of Hg species in biota, sediment and water [15]. Volatile species, such as Hg(0) and DMHg, are usually purged from water samples and trapped on gold and carbo traps before detection. Hg(II) is usually measured as the fraction that is readily reduced to Hg(0) by tin chloride (SnCl₂), while total Hg (THg) determination involves decomposition of Hg species, by oxidation with bromine chloride (BrCl) or UV irradiation, to Hg(II) which is subsequently reduced to Hg(0). MMHg undergoes derivatization using ethylating or propylating agents to volatile ethylmethylmercury or propylmercury before purging and trapping on Tenax traps. An extraction step is usually required prior to derivatization to liberate the MMHg cation
(CH₃Hg⁺) from the sample matrix and this is usually achieved by acid or alkaline extraction followed by extraction into an organic solvent or by steam distillation. A combination of a separation technique, such as gas or liquid chromatography (GC or HPLC), with selective detectors, such as electron capture, atomic emission spectroscopy (AES), atomic absorption spectrometry (AAS), atomic fluorescence spectroscopy (AFS), or inductively coupled plasma mass spectrometry (ICP–MS) is used for actual measurement of Hg species. Among the methods mentioned, the coupling of GC to ICP–MS combines high sensitivity with the possibility of species specific isotope dilution measurements to evaluate specific sample-preparation steps [36]. Isotope dilution which involves the addition of one or more isotopically labelled Hg tracers of different molecular structure enables the identification and correction of both species specific and matrix dependent losses and transformations occurring in individual samples. ICP-MS is a very powerful tool and is being increasingly used in research studies as it offers exceptionally low detection limits and allows the precise measurement of Hg isotopes. ICP-MS also offers new opportunities, not available with other techniques, such as the use of multiple stable tracers in experiments to study the fate and simultaneous transformation of Hg species in the environment and biological systems [37-40].

**Hg global emission**

Mercury enters the global environment from natural and anthropogenic emissions to the atmosphere. Degassing from rock weathering and geothermal activities are the main natural sources of Hg. Hg emitted from land and oceans consists of natural Hg and previously deposited Hg, which is of both natural and anthropogenic sources. Since the onset of the industrial revolution in the 1850s, anthropogenic Hg activities have mobilized vast
quantities of mercury from a relatively inert state in the Earth’s crust and redistributed it throughout the more biologically active and mobile compartments of the environment (surface soils, atmosphere, lakes, rivers, oceans). Anthropogenic Hg contributions to the environment have increased dramatically, with enrichment estimations of 25% in surface ocean waters and 300 – 500% in the atmosphere [41]. Consequently, atmospheric Hg deposition has increased by two to four fold ([29] and references therein) disrupting its cycle and increasing its level in water, air and soil.

Today, the global emissions of Hg, from both natural and anthropogenic sources, are estimated between 6900 and 7500 t y\(^{-1}\) [42-44]. Natural Hg emissions, which include reemissions of previously deposited Hg is estimated to range between 4510 to 5207 t y\(^{-1}\) [42-44]. The main uncertainty in Hg natural emissions is associated with re-emissions, which varies between 30% [43] to 56% [42] of global Hg emissions. Although the original source of reemitted Hg cannot be determined with certainty, evidence of the contribution of anthropogenic activities suggests that most of the re-emitted Hg was originally from anthropogenic sources [45-47]. Oceanic Hg emissions represent 38% to 52% of natural Hg emissions [42-44], while emissions from terrestrial surface account for 33% and the remaining relatively small contribution from primary natural sources such as biomass burning (13%) and volcanoes (2%) [44].

Anthropogenic Hg emissions, from models as well as inventories, are estimated between 1900 and 2600 t y\(^{-1}\) [42-44, 48, 49] representing roughly 30% of the global Hg emission. According to an inventory made for 2005, fossil fuel combustion (46%) is the main contributor to anthropogenic Hg emissions followed artisanal and small scale gold mining (ASGM) (17%) [50]. However, a more recent estimation made in 2010 shows a lower contribution of fossil fuel combustion (24%) due to increased estimates from ASGM (37%)
and improved combustion efficiency and emission controls worldwide, despite the construction of new coal fired power plants. The other anthropogenic sources include non-ferrous metals production (10%), cement production (9%), waster products (5%) and large scale mining (5%) [4].

Asian countries contribute about 50% of the global anthropogenic emissions with China accounting for roughly 30% of the global anthropogenic emission. The African continent is the second most important contributor (17%) followed by South America (12.5%). Anthropogenic emissions from Europe (10.8%) and North America (3.1%) are relatively low due to efforts to reduce Hg emissions [4].

**Mercury contamination and toxicity**

The main environmental problem associated with mercury emissions is the transformation of Hg to MMHg, its most toxic form. MMHg, is found predominantly in aquatic environments and is the main form (> 75%) of Hg in aquatic organisms [51, 52] as it has the capacity to efficiently bioconcentrate in biota and biomagnify through the aquatic food chain. Nowadays, the consumption of marine products mostly fish is the main route of exposure to MMHg for humans [53, 54].

The neurotoxicity of Hg [55] has been recognized following disastrous episodes of Hg poisoning resulting in serious diseases and mass health disasters. The most severe Hg poisoning episode occurred in 1956 in Minamata, Japan, after the contamination of the seafood supply of an entire fishing village with MMHg by a nearby industry [56, 57]. Another tragic epidemic occurred in 1971 and early 1972 in Iraq, when families of farmers consumed seed dedicated for planting and treated with methyl and alkyl Hg despite written warnings of Hg toxicity [57, 58]. These contamination incidents raised concerns about the
adverse environmental and health effects of Hg resulting in increasing studies on the geochemical cycle of mercury, its sources and sinks and its transport through the environment.

MMHg neurotoxicity symptoms in adults causes impaired cardiovascular health as well as sensory (e.g. ataxia, loss of muscle control), auditory and speech disorders (dysarthria) [53]. Developing foetus are also exposed to MMHg which is actively transferred across the placenta via neutral amino acid carrier system [59] during pregnancy. MMHg is also present in maternal milk [53, 60] and transmitted to newborns through breastfeeding causing long-term impaired neurological development and cognitive changes in infants [53, 55]. Hg toxicity in animals is mainly manifested by reduced reproduction rate and other behavioral, neurochemical and hormonal changes that poses a threat to the survival of species [61].

Since Hg has been recognized as a toxic pollutant and under the impulse of the world health organisation (WHO) [62], there are nowadays worldwide advisories [63-66] for individual at risk such as pregnant women or of child bearing age and infants to either limit their fish consumption to a few meals per week or to select fish species known to have low levels of MMHg (non-predatory fish). During the past decades, efforts have been made to reduce the industrial use and emissions of Hg through better emission control legislation, improved technology, product switch outs, and reduction of industrial pollution. Furthermore, in an effort to reduce risk associated with human and wildlife Hg exposures, the Minamata convention on Mercury, which is a legally binding instrument towards the global reduction of anthropogenic Hg exploitation and emissions, prepared by the United Nations Environment Program (UNEP) was adopted and signed in October 2013 and is currently being ratified [67].
Biogeochemical Hg transformation

Hg cycles through environmental compartments and is subject to a series of biogeochemical transformations which alter its chemical and physical properties, which determines its fate and its toxicity in the environment. The main transformations of Hg are oxidation to reactive Hg(II), reduction of Hg(II) back to Hg(0), methylation of Hg(II) to methylated Hg species mainly MMHg and DMHg and the demethylation of methylated Hg species to Hg(II) and Hg(0). However, despite concerns related to MMHg bioaccumulation in fish and other seafood products, we still have an incomplete understanding of the mechanisms and factors controlling the formation and destruction of MMHg. The current knowledge of the chemical (abiotic) and biological (biotic) mechanisms affecting Hg transformations i.e., oxidation and reduction, methylation and demethylation, is discussed below. Figure 1-1 provides a schematic overview of the main transformation pathways predominant in air and water.
Figure 1-1. Hg biogeochemical transformations in the atmosphere and aquatic environments. Solid arrows indicate major processes, while dashed arrows indicate reactions of minor or uncertain importance.
**Oxidation of Hg(0)**

Oxidation, which is the transformation of Hg(0) to Hg(II), occurs in various environmental compartments such as the atmosphere [68, 69], snow [70], marine [71] and freshwater [72] systems, and is believed to be both microbially [73, 74] and photochemically [75] mediated.

In the atmosphere, Hg(0) oxidation is believed to occur in gas, aerosol and aqueous (in fog or cloud droplets) phase and is primarily abiotic, driven by light mediated reactions with oxidants. Ozone (O₃) has for long been proposed as the main oxidant for the oxidation of Hg(0) in both the gaseous [76] and aqueous [69, 77] phase. However, the faster kinetics of Hg(0) oxidation by halogen radicals such as bromine (Br•) [78, 79], chlorine (Cl•) [78, 80] and hydroxyl (OH•) [81, 82] suggest that these pathways might be more important. The diurnal pattern exhibited by Hg(II) in the atmosphere, with maximum concentrations at midday [9, 83] confirms that Hg(0) oxidation is controlled by photochemistry.

Photoinduced oxidation of Hg(0) also has been demonstrated in aquatic environments. In estuarine ecosystems, Hg(0) oxidation was found to be chiefly mediated by UV radiation involving reactions with intermediate photoproduced oxidant(s) such as OH• [75]. In marine waters, the oxidation of Hg(0) is believed to be enhanced by halides such as chloride and appropriate particle surfaces and thus of importance in coastal regions where particulate matter loadings are higher [71, 84]. Biotic mercury oxidation has been reported in freshwaters and is attributed to bacterial enzymatic activity, induced by hydrogen peroxide mediating the oxidation reaction [72, 85]. It has also been demonstrated that Hg(0) oxidation occurs even under dark conditions and is favored by biogenic organic materials [73]. A recent study demonstrated active as well as passive oxidation of Hg(0) to Hg(II) by anaerobic bacteria [74].
Reduction of Hg(II)

Reduction, the transformation of Hg(II) to Hg(0) is the main process controlling the evasion of Hg to the atmosphere from water, ice, snow or soil. Hg(II) reduction plays an important role in the biogeochemical cycling of Hg in aquatic systems as it controls the concentration of Hg(II), the substrate for MMHg methylation, as well as the formation of Hg(0) which is readily evaded to the atmosphere. Reduction reactions are mediated by both abiotic and biotic processes. Abiotic reduction of Hg(II) in the presence of sunlight and in association with dissolved organic carbon (DOC) has been demonstrated in lakes [86] as well as seawater [71, 87]. The efficiency of the photoreduction is influenced by levels of reducible Hg(II) complexes and radiation wavelength (particularly UV-A and UV-B) and intensity. Photoreduction is also affected by DOC, since higher photoreduction rates have been reported in clear, low DOC lakes [88]. DOC, at high concentrations, is believed to form non-photoreducible Hg (II) complexes [88] but may also act as a competitive inhibitor for solar radiation, scavenging UV radiation before it can photoreduce Hg(II) [84].

Production of Hg(0) from snowpacks has been attributed to photodegradation of Hg(II), which is mainly mediated by UV-B irradiation [89-91]. Although not completely understood, the mechanisms proposed for Hg photoreduction are (i) direct photoreduction of Hg(II) complexes or DOC-bound Hg, (ii) reduction by photoreduced Fe, Mn or humic acids during their reoxidation or (iii) enzymatic reduction by photosynthetic phytoplankton and cyanobacteria [84]. Even though reduction of Hg(II) to Hg(0) is believed to occur in the atmosphere, very little is known about the mechanisms. Hg(II) reduction in the aqueous phase, with dissolved sulfite (SO$_3^{2-}$) as the main reducing agent, has been proposed [92] but is believed to be of limited importance due to the preferential formation of other
complexes such as HgCl$_2$ [29]. Photoreduction of gaseous Hg(II) has been hypothesized [6] but the exact mechanism is unknown and requires further investigation.

Biotic Hg(II) reduction is mediated by mercury resistant bacteria possessing the mer operon (merA genes) coding for the enzyme mercury reductase ([93] for a review). Biotic reduction has been reported in boreal lakes [72] as well as high Arctic marine environment [94] highlighting the importance of microbial Hg(II) reduction in the biogeochemical cycling of Hg in these ecosystems. In open ocean, biotic reduction is suspected to be of greater significance in deeper waters even though it is believed to occur in surface water also [95].

**Methylation**

Methylation, the conversion of inorganic Hg(II) to methylated Hg species, is a key step for the entrance of Hg into the food chain. Methylation occurs mainly in aquatic environments under anoxic as well as oxic conditions producing MMHg and DMHg [96]. Methylation has been reported in lake sediments [12, 97-99], periphyton of macrophytes [100], in the water column of lakes [101, 102] as well as ocean surface waters [103, 104]. Microbial activity is believed the main mechanism responsible for methylation [11], although abiotic methylation is possible [14]. The main microorganisms identified for the biotic methylation of Hg are sulphur reducing bacteria (SRB) [12, 105-108] and iron reducing bacteria (IRB) [109]. Other organisms are believed to methylate Hg(II) although potential methylators such as methanogens have been reported so far to be of minor significance [12, 97, 105]. The proposed mechanisms for Hg(II) methylation include methylation mediated by a series of enzymatic reactions involving acetyl coenzyme A (CoA) synthesis and methyl group transfer via methylcobalamin [110] and the involvement
of methyltranserases in Hg methylation [111]. A recent study has demonstrated that a two-gene cluster encoding for a methyl carrier and an electron donor required for corrinoid cofactor reduction were responsible for Hg methylation in SRBs [106].

Abiotic methylation of Hg(II) has been proposed in in the presence of methyl donors such as methylcobalamin, methyltin compounds, and dissolved organic matter components namely humic and fulvic acids. Transmethylation from humic acids is potentially the main abiotic mechanism in water and sediments due to the high concentrations [14, 112]. Abiotic methylation of Hg(II) by acetic acid has been shown to be kinetically [113] feasible and proposed for aqueous MMHg production in the atmosphere [114]. However, the general consensus is that abiotic methylation is insignificant under natural conditions [14, 113, 115]. Less information is available on the synthesis mechanism of DMHg. The biogenic production of DMHg (as dimethylmercury sulfide) from interactions between MMHg and hydrogen sulphide (H$_2$S) under anoxic conditions has been proposed [116].

The extent of biotic methylation is determined by the availability of the Hg(II) substrate as well as microbial activity and community structure. The main environmental factors controlling Hg methylation include temperature, pH, redox potential, nutrient content, sulfur speciation and the presence of inorganic and organic complexating agents [5, 7, 96, 117]. MMHg formation is favored under low pH conditions presumably due to the dominance of Hg methylation bacteria over other microbes and/or higher Hg(II) bioavailability under such conditions ([5] and references therein). Furthermore, increased release of MMHg from sediment and reduced binding of MMHg with humid acid were observed at decreasing pH explaining partly high Hg concentrations in fish from low pH lakes ([7] and references therein). Laboratory tests revealed maximum abiotic MMHg production at pH 4.0 – 4.5 [112] while volatilization of freshly synthesized DMHg was
observed at pH 6.2 – 6.5 [116]. Sulfate concentration is a critical parameter controlling biotic methylation as sufficient sulfate is required for microbial (SRBs) activity, while the product of microbial sulfate reduction, sulfide, affects Hg(II) availability by forming HgS precipitation [97]. Hg(II) availability is also controlled by complexating agents such as dissolved organic carbon (DOC), which on one hand binds with Hg(II) reducing its bioavailability for methylation reactions [118] but on the other hand enhances Hg(II) mobility, transporting it to methylation sites. Furthermore, DOC enhances biological activity serving as a substrate for microorganisms ([5] and references therein). Microbial activity is also influenced by nutrient supply and temperature ([5, 117] and references therein).

**Demethylation**

Demethylaton, i.e., the decomposition of methylated Hg species by photochemically and biologically mediated processes, is another crucial transformation controlling levels of both MMHg and DMHg in aquatic environments. Biotic demethylation is mediated by oxidative and reductive pathways. Reductive demethylation is mediated by bacteria possessing the mer operon producing enzymes organomercurial lyase (merB) [119] and mercuric reductase (merA) that catalyze the cleavage of the Hg-C bond and subsequent reduction of Hg(II) respectively, producing methane and volatile Hg(0) as end products [93, 120]. Oxidative demethylation occurs via biochemical pathways where bacteria, mainly methanogens and sulfate reducers, convert the methyl group of MMHg producing carbon dioxide and Hg(II) [121, 122]. Reductive demethylation is believed to be dominant in highly contaminated and freshwater systems while oxidative demethylation dominate at non elevated MMHg concentration [122] and in marine environment [121]. While biotic
demethylation has been demonstrated in sediment, non-biological demethylation by photochemical processes is believed to be the most important sink for MMHg and DMHg in surface waters. Abiotic photochemical demethylation occurs by the cleavage of the carbon-Hg bond by UV radiation as well as visible light, forming either Hg(0) or Hg(II) [123-125]. Generation of reactive singlet oxygen generated by photolysis of dissolved organic carbon has been proposed as the driving mechanism for photodecomposition [126]. Furthermore, it has been demonstrated that the rate of MMHg degradation depends on the binding ligand. MMHg bound to sulphur containing ligands is less stable than methylmercury-chloride complexes, which are more abundant in marine waters [126]. Gas phase demethylation of DMHg has been demonstrated by reaction with atomic chloride [18] and hydroxyl radicals [19] producing MMHg, while oxidation of DMHg with nitrate radicals is believed to produce Hg(0) as the main product [127].

**Cycling of Hg species in marine ecosystems**

Atmospheric transport has been identified as the major pathway in the worldwide distribution of mercury in the environment. In the atmosphere, successive oxidation and reduction transformation drives the transport as well as the extent of deposition. In oceans, oxidation and reduction controls volatilization to the atmosphere, while methylation and demethylation reactions control the formation of MMHg and thus, the bioaccumulation of Hg. The ocean is considered a sink as well as a source of atmospheric Hg due to the deposition of Hg(II) on ocean surfaces, where it is partly reduced to Hg(0) and re-emitted back to the atmosphere. Aquatic ecosystems seem to be most susceptible to MMHg contamination, as they are subject to atmospheric Hg deposition and are the main sites of Hg methylation forming toxic MMHg.
**Mercury in the atmosphere**

**Elemental and reactive Hg**

Hg(0) or GEM, is the most abundant species in the atmosphere (> 95%) [29] with an average concentration of 1.7 ng m⁻³ (range 1.2 ng m⁻³ to 1.8 ng m⁻³) in the northern hemisphere [29, 83, 128-131]. Hg(0) is very stable and uniformly distributed in the atmosphere with a residence time estimated between 0.7 to 1.4 years [43, 76, 132-134]. Due to its persistence in the atmosphere, Hg(0) can be transported by air masses over long distances to remote and pristine areas such as the poles. Hg(II) or RGM, has relatively short residence time (days to weeks) in the atmosphere due to its high wet and dry deposition velocities [9, 135]. RGM and PHg, which consists of Hg(II) and Hg(0) adsorbed on particles, are usually deposited close to their sources of emission [29]. RGM and PHg are present at much lower concentration ranging from 2 pg m⁻³ to 18 pg m⁻³ and 3 pg m⁻³ to 26 pg m⁻³, respectively [83, 128, 129, 131] showing great variability. The oxidation of Hg(0) in the atmosphere is an important mechanism as it is the main sink of Hg(0) and governs the deposition of Hg(II). Oxidation of Hg(0) in the atmosphere may, to some extent, be balanced by simultaneous aqueous-phase reduction of Hg(II) but it is believed to be of minor importance at a global scale [6, 29]. Oxidized Hg is removed from the atmosphere through the wet (rain or snow) and dry (particles and aerosols) deposition of Hg(II) to ocean surfaces where it can be methylated to bioavailable MMHg (Figure 1-1).

**Methylated Hg species in the atmosphere**

The presence of methylated Hg species in air has been difficult to determine due the analytical challenge of measuring suspected low concentration (pg m⁻³). Despite the paucity of information on methylated Hg speciation in the atmosphere, both MMHg and DMHg
are suspected to be present in air, especially over water bodies. Indeed, emissions of DMHg to the atmosphere have been reported over contaminated sites [136] as well as over the Atlantic Ocean [137], Arctic and Antarctic Oceans [138] suggesting that it is of oceanic origin. MMHg has also been reported in urban air [31, 32] as well as in precipitation over the Pacific Ocean [139, 140], temperate [141], boreal [142] and high Arctic lakes[143] and in snow in coastal Arctic [144, 145] and at high altitude [146]. Even though little information is available on MMHg and DMHg in the atmosphere, methylated Hg species are suspected to exist at trace levels (a few pg m^{-3}). The lifetime of MMHg in the atmosphere is estimated to be a few days (~ 9 days) as it is suspected to be rapidly deposited to oceans and other surfaces due to scavenging by aerosols (e.g., sea spray) or precipitation (e.g., coastal rainwater or fog). MMHg is also believed to be susceptible to photodegradation to Hg(II) in aqueous conditions [82]. Kinetic reactions between DMHg and radicals [18, 19, 147] suggest that DMHg has relatively shorter residence time (a few hours to days) in the atmosphere and most likely degrades to MMHg [18, 19]. The sources of atmospheric MMHg and DMHg are still unclear. DMHg in the atmosphere is suspected to be produced in marine waters [138, 148] from which it volatizes rapidly due to its high vapour pressure (Table 1-1, Figure 1-1). DMHg flux from open oceans has been estimated between 0.03 to 0.95 ng m^{-2} hr^{-1} in the Pacific Ocean [149] and between 4.8 and 27.3 ng m^{-2} hr^{-1} in the Arctic Ocean [145, 150]. The degradation of marine derived DMHg to MMHg has been proposed as a source of MMHg in the atmosphere. This has been suggested following the report of elevated MMHg concentrations in snow close to polynyas in the Arctic and the positive correlation with chlorine [144]. This hypothesis is supported by laboratory experiments which demonstrated the rapid degradation of DMHg to MMHg in the presence of Cl atoms and OH radicals [18, 19]. The abiotic methylation of Hg(II) to MMHg in the atmosphere
by methylators such as acetate has also been suggested [114]. Laboratory test revealed that even though the reaction is possible, it accounts for only a small fraction of total MMHg in precipitation [113] suggesting other pathways for MMHg production in the atmosphere. Further studies are needed to identify the potential sources and importance of methylated Hg species in the atmosphere.

**Mercury in aquatic environment**

The main source of Hg to natural waters is wet and dry atmospheric deposition of Hg(II) [43, 151]. Other sources of Hg to aquatic systems include riverine inputs which can be significant in coastal regions and on a regional scale for example in the Arctic Ocean [152, 153]. Deposited Hg(II) is either (i) reduced to Hg(0) which is rapidly re-emitted back to the atmosphere, (ii) scavenged by particles to deeper waters for sequestration in sediment or (iii) incorporated by the biological cycle of Hg after methylation.

The re-emission of deposited Hg(II) from aquatic surfaces to the atmosphere is driven by the balance between simultaneous oxidation and reduction reactions which controls the production of Hg(0). Natural waters are usually supersaturated in Hg(0) relative to the atmosphere, resulting in the flux of Hg(0) to the atmosphere [84] which often exhibits a diurnal pattern [72, 113].

While deposited Hg enters the aquatic environment mainly as Hg(II), it is as MMHg that Hg is accumulated in organisms stressing the need for a good understanding of the factors and processes controlling MMHg production in aquatic systems. The major features of the aquatic-biological cycle of mercury are the formation of methylated Hg species namely MMHg and DMHg, the uptake of MMHg in biota and its biomagnification along the food-chain. The destruction (demethylation) of methyl mercury is also an important component
controlling the concentration of MMHg that is available for uptake. MMHg biomagnifies by more than a million fold in aquatic environments from relatively low concentrations in water (pg L\(^{-1}\)) to elevated levels in fish (> 0.5 µg g\(^{-1}\)) that represent a health threat to humans if consumed regularly [63, 64]. Biomagnification is most important at the base of the food chain, where MMHg is assimilated from water by phytoplankton and efficiently transferred to higher organisms along the food chain [154], resulting in higher concentrations in predators than in preys. The key factor determining the concentration of mercury in biota is the concentration of MMHg in aquatic systems, which is controlled by the relative efficiency of methylation and demethylation processes. The rates of formation and destruction of MMHg are therefore of prime importance for the bioaccumulation of Hg in aquatic organisms.

*M Mercury methylation and demethylation in water*

Although not fully understood, it seems that the mechanisms of methylation and its products are not the same in fresh and marine waters. In freshwater systems, methylation, producing primarily MMHg, occurs in anoxic hypolimnetic waters [102, 155] and in sediment [12, 98, 156] and is mainly biologically mediated with SRBs as the principal methylators [12]. In marine systems, methylation in sediment is an important source of MMHg in estuaries, coastal environments and continental shelf [105, 157, 158]. However, in open ocean, methylation is believed to occur throughout the water column with maximum production of methylated Hg species at the oxygen minimum zone (OMZ) in association with organic matter regeneration is more significant. Indeed, elevated concentrations of both MMHg and DMHg have been reported at the OMZ in south and equatorial Atlantic [159, 160], North Atlantic[161], Pacific [162, 163] and Mediterranean
oceans. Similar patterns were observed in the Arctic Ocean where elevated methyl Hg concentrations have been reported at mid depth [150] and in the OMZ [165]. The relative predominance of DMHg in marine systems, suggests that it is the main product of methylation [159, 166]. Furthermore, laboratory cultures demonstrating the production of both MMHg and DMHg by polar marine bacteria [138] and microalgae [148] as well as link between biomass and DMHg and its predominance under high bioactivities in the water column [167] strongly support the hypothesis that DMHg is of biogenic origin and the main product of methylation in marine systems. Highest DMHg concentrations (range: ~3 pg L$^{-1}$ to 65 pg L$^{-1}$) are often found in subthermocline and deep waters while lowest concentrations are found in surface waters (e.g. [150, 159, 161, 162]). The depletion of surface water with DMHg suggests its photodegradation as well as evasion to the atmosphere due to its high volatility. Light mediated degradation of methylated Hg species to Hg(II) which is ultimately reduced to Hg(0) has also been demonstrated in lake water [123, 125, 168] as well as in marine waters, e.g. [103]. DMHg is believed to be more stable in deep ocean waters than in shallow waters since it is the predominant methylated Hg species and its degradation to MMHg and Hg(0) seems slower [159, 166]. The sources of MMHg in ocean surface water are still unclear. MMHg is predicted to be a breakdown product of DMHg [159, 166] and DMHg demethylation to MMHg in surface water has been proposed as an important mechanism for the presence of MMHg in surface water. Unfortunately, very little information is available on the fate of DMHg in the marine ecosystems. Apart from production as a result of DMHg demethylation other proposed sources of MMHg include river inputs, transport by ocean currents and upwelling, in situ methylation and atmospheric deposition. River inputs of MMHg is of significance on a regional scale and account for only a fraction of surface MMHg [153], while the
contribution of ocean currents is suspected to be negligible due to the short aqueous lifetimes of MMHg compared to ocean mixing time scales (500-1000 years) [169]. Recent work has demonstrated the methylation of Hg (II) to both MMHg and DMHg in surface and subsurface waters of the Arctic Ocean [104] and MMHg production from Hg(II) in Mediterranean surface waters [103]. These findings suggest that other unidentified processes or microorganisms other than SRB are responsible for MMHg production in surface waters. The contribution of atmospheric deposition to oceanic MMHg pool has not been evaluated despite records of MMHg in precipitation mainly due to uncertainties regarding the presence of methylated Hg in the atmosphere. The above uncertainties demonstrate the need to identify the factors controlling the production of MMHg but also the importance of DMHg as a source of MMHg. Indeed, despite the fact that is it not bioaccumulated [170, 171], DMHg seems to be a precursor for MMHg both in the water column and the atmosphere and might thus play a crucial role in the exposure of biota to Hg.

**Hg contamination in the Arctic**

There are virtually no point sources of Hg in the Arctic (see Figure 1-2 for a map) and, yet, Hg contamination in this remote part of the world poses serious human health threats and ecological risks. Hg in the Arctic is mainly from anthropogenic origin and it has been demonstrated that concentrations of Hg (as MMHg) in Arctic biota have increased significantly since the onset of the industrial revolution [45]. Hg contamination in the Arctic is linked to the global Hg cycle as Hg is transported to this region of the world mainly via air currents, ocean currents, and rivers (Figure 1-3). Long range transport of contaminated air masses is the main mechanism for Hg delivery in the Arctic as it occurs
much faster (within weeks) than via transport by ocean currents (decades). Hg moves in the atmosphere by a series of deposition and volatilization events referred to as the grasshopper effect similarly to persistent organic pollutants (POPs). Hg inputs to the Arctic via air have been estimated to 100 t y⁻¹ while the Arctic Ocean accumulates 25 t y⁻¹ [50].

The oxidation of Hg(0) and its subsequent deposition in the Arctic is enhanced at the onset of polar spring due to the prevailing climatic and atmospheric conditions resulting in Atmospheric Mercury Depletion Events (AMDEs). During AMDEs, there is depletion of Hg(0) in the atmosphere (< 0.1 ng m⁻³) due to its rapid oxidation to Hg(II) by reactive halogens such as Cl⁻ and Br⁻ [68, 133]. Newly formed Hg(II) is rapidly and massively deposited on surfaces, and if not reduced to Hg(0) and re-emitted back to the atmosphere [70, 172], it can be transformed to toxic and bio-accumulative MMHg. Methylation of Hg(II) occurs mainly in the Arctic aquatic environments resulting in MMHg biomagnification along freshwater and marine food webs (Figure 1-3). Concentrations of Hg in the arctic marine organisms are among the highest in the world [50, 52, 173] and often exceed the concentration deemed safe for human consumption (0.5 µg g⁻¹). Arctic populations are exposed to Hg through the consumption of marine fish and mammals, including ringed seals, belugas and polar bears, which is an integral part of their subsistence living and traditional diet [174, 175].

Today, the Arctic ecosystem is most vulnerable to Hg contamination as concentrations in biota are already above threshold levels [45, 50]. Furthermore, inputs of Hg to Arctic ecosystems are expected to increase due to increasing release and long range transport of Hg from lower latitudes but also increasing local anthropogenic activities e.g., industrial and demographic development, increasing mining activities oil and gas exploration and production [50]. In addition to increasing Hg inputs, the rapidly changing climate is likely
to result to greater mobilisation of Hg in the Arctic [176, 177]. These observations demonstrate the need to better understand the factors affecting the accumulation of Hg in this fragile ecosystem.
Figure 1-2. Map of the Arctic showing the population settlements. The study was conducted in the Canadian Arctic namely in Hudson Bay and the Canadian Arctic Archipelago. Adapted from UNEP 2013 [178].
Figure 1-3. A simplified schematic diagram showing the delivery of mercury (Hg) from lower latitudes to the Arctic where it is bio-accumulated in biota. Hg(0): gaseous elemental Hg, Hg(II): reactive gaseous Hg, MMHg: monomethylmercury. Adapted from: Macdonald et al., 2005 [176]
Hypotheses and objectives

The atmosphere is deemed to be a major pathway for Hg introduction into the Arctic environment, but considerable knowledge gaps still exist on the pathways and delivery processes of MMHg to the aquatic ecosystem. From the synthesis of current knowledge and gaps on the presence and cycle of methylated Hg species in the Arctic marine ecosystem, I hypothesize the following:

1. Methylated mercury species (namely MMHg and DMHg) are present in the Arctic marine boundary layer (i.e., the part of the atmosphere that has direct contact and hence, is directly influenced by the ocean) and atmospheric deposition is a source of MMHg to surface water.

2. *In situ* methylation of Hg(II) to MMHg occurs in surface water and is a source of MMHg in surface water

3. DMHg which is also produced by Hg(II) methylation in water, is degraded to MMHg contributing to the pool of MMHg in surface water

The general objective of the research presented in this thesis is to establish sources and fate of toxic MMHg in the Arctic marine ecosystem and identify biogeochemical processes and factors controlling the production and destruction of methylated Hg species in the Arctic Ocean. In order to test the above hypotheses my research addressed the following:

1. Development and optimization of a method for the sampling of MMHg and DMHg in the atmosphere.

2. Measurement of methylated Hg species concentrations in the Arctic Ocean marine boundary layer
3. Investigation of Hg methylation and demethylation potential of Hg species in the Arctic Ocean surface water.

**Approach**

Firstly, I tested the suitability of commonly used and new adsorbents for the preconcentration of MMHg and DMHg. The evaluation examined trapping efficiency, adequate sample preservation during storage and maximum overall recovery. A sampling method for the measurement of methylated Hg species in air was developed and validated. I participated in two sampling campaigns on board the research icebreaker, CCGS Amundsen, in summer 2010 and 2011. The presence and spatial distribution of MMHg and DMHg in Hudson Bay and the Canadian Arctic archipelago marine boundary layer was investigated and the factors controlling the presence of these two methylated Hg species were examined. Water samples were collected and shipboard incubation experiments using isotopically enriched Hg species were conducted to determine Hg methylation and demethylation rates and transformation mechanisms of methylated Hg species. The importance of in situ methylation of Hg(II) to MMHg as well as the demethylation of DMHg, which is also produced during methylation, as sources of MMHg in surface water was investigated. Finally, oceanographic parameters were evaluated and geochemical processes influencing the production and loss of methylated Hg species were investigated.
Overview of following chapters

The presence of methylated Hg species in the Arctic Marine Boundary Layer (hypothesis 1) will be discussed in Chapter 2 and 3. Chapter 2 evaluates solid adsorbents for the trapping and recovery of methylated Hg species from gaseous samples and the optimized conditions for air sampling are established as a first step for the actual measurement of methylated Hg species over the Arctic Ocean which is presented in Chapter 3. Chapter 4 investigates mercury methylation and demethylation potentials in Arctic Ocean surface water as well as the products of these transformations and their controlling factors (hypotheses 2 and 3).
Literature Cited


155. Zheng, J. and H. Hintelmann, *Hyphenation of high performance liquid chromatography with sector field inductively coupled plasma mass spectrometry for the determination of ultra-trace level anionic and cationic arsenic compounds*


CHAPTER 2: EVALUATION AND OPTIMIZATION OF SOLID ADSORBENTS FOR THE SAMPLING OF GASEOUS METHYLATED MERCURY SPECIES
Abstract

This study evaluates the suitability of commercially available adsorbents for the measurement of gaseous organic mercury species namely monomethylmercury (MMHg) and dimethylmercury (DMHg).

Bond Elut ENV (BE), a new generation of divinylbenzene (DVB), is evaluated the first time for simultaneous sampling and quantification of ultra-trace levels of MMHg and DMHg in air and its performance compared against Carbotrap® B (CB) and Tenax® TA (TA), two commonly used adsorbents for mercury solid phase adsorption.

The suitability of TA as an absorbent for MMHg (recovery 100 ± 8.1 %) but less so for DMHg (recovery 64 ± 17.3 %) was confirmed while the reverse was observed for CB with an average recovery of 100 ± 0.3 % for DMHg but only 61 ± 32.5 % for MMHg. BE is the only adsorbent that showed excellent performance for trapping both Hg species with recoveries of 98 ± 9.2 % and 95 ± 8.1 % for MMHg and DMHg, respectively. Furthermore, BE exhibited much higher sampling capacities (> 100 L at 4 °C) and preservation of sample integrity (> 1month at -20 °C in the dark).

Overall, BE proves to be the most suitable adsorbent for simultaneous trapping of organic Hg species with high sampling capacity and sample stability but also very good chromatographic properties which are desirable characteristics for both collection traps and analytical traps. Bond Elut ENV is proposed as an alternative to both Tenax® TA and Carbotrap® B with additional advantages of offering more versatility and sampling options. Keywords: Monomethylmercury, Dimethylmercury, solid phase adsorption, Bond Elut ENV, Tenax® TA, Carbotrap® B, air sampling
Introduction

Mercury (Hg) is a potent neurotoxin [17, 55] that bioaccumulates and biomagnifies in biota in its organic form monomethylmercury (MMHg). MMHg and dimethylmercury (DMHg), another important organic Hg species, are formed by methylation of inorganic reactive mercury (Hg$^{2+}$) by biotic and to a lesser extent abiotic processes. Biotic methylation are mediated by microorganisms, mainly sulphur reducing bacteria [12, 105, 138] and iron reduction bacteria [109] in anoxic aquatic environments at the sediment-water interface [12, 105, 108] and in the water column [101, 104]. Consequently, the consumption of marine food, mainly piscivorous fish is the most common Hg exposure pathway [84, 154, 179] for humans.

In aquatic systems, MMHg is bioactive and as a cation (MeHg$^+$) usually binds to and forms complexes with inorganic (e.g. Cl$^\text{−}$, Br$^\text{−}$, OH$^\text{−}$) or organic ligands (e.g. in dissolved organic matter – DOM) [5]. DMHg on the other hand, is unreactive and is either rapidly converted to MMHg thus contributing to the MMHg pool or volatilized to the atmosphere [166, 180-183]. DMHg in the atmosphere is however unstable and photodegrades to MMHg or Hg$^{2+}$ [159]. DMHg might thus an important pre-cursor of MMHg in marine environments. Furthermore, MMHg has been recorded in precipitation [114, 139, 141, 142, 146, 184, 185] suggesting the presence of MMHg in the troposphere resulting either from DMHg demethylation [18, 19] or acetate mediated atmospheric methylation of Hg$^{2+}$ [113] or both. These studies converge to suggest that both DMHg and MMHg are present in the atmosphere and can be a source of MMHg to open water.

Mercury speciation inventories at the water-air interface are thus crucial for a better understanding of the transformation mechanisms and sources of MMHg in surface water.
Unfortunately, very little is known about the presence of organic Hg species in the atmosphere. Their detection and quantification in air remains an analytical challenge due to the suspected trace concentrations (pg m$^{-3}$). A few successful attempts to measure one or both species in controlled environments [25, 31, 32, 186] or in areas with elevated organic Hg concentrations, such as floodplains [187] and landfills [136], have been reported but to the best of our knowledge, no analytical method is available for routine measurement of organic Hg in air.

Organic Hg species from aqueous samples are commonly measured by pre-collection on solid adsorbents (purge-and-trap) and quantified by either cold-vapor atomic fluorescence spectrometry (CVAFS) [25] or inductively coupled plasma mass spectrometry (ICPMS) [98] after thermodesorption and separation by gas chromatography (GC). The main advantage of this method is its very low detection limit since solid adsorbents have relatively low background and risks of contamination due to added reagents or other sample manipulations are minimal. Furthermore, solid phase adsorption is convenient and reliable as adsorbent traps deliver very good reproducibility and can be reused several times before renewal. Disadvantages are (i) low sampling volumes thus limiting maximum achievable preconcentration factors when analyzing samples with ultra-trace levels of Hg such as ocean water or air samples but also (ii) variability in adsorbent trapping efficiencies preventing a simultaneous precise and accurate measurement of both MMHg and DMHg.

To overcome these limitations, this study presents an evaluation of commercially available solid adsorbents for collecting and measuring volatile organomercury compounds. The performance of adsorbents under various sampling and storage conditions is assessed and optimum conditions are identified. The applicability of solid adsorbents for
preconcentration of both MMHg and DMHg from air samples by active sampling is also discussed.

**Methodology**

**Adsorbents**

Criteria for the selection of adsorbents were their (i) thermostability, i.e. no degradation or artifact formation during desorption, (ii) strength of interaction with Hg species (MMHg and DMHg) to allow proper trapping but at the same time complete recovery at moderate desorption temperatures, and (iii) surface area so that fairly large volume of air could be sampled without breakthrough. The affinity for moisture was also considered to minimize interferences during preconcentration and analysis. Based on these criteria, the solid adsorbents preselected for organic Hg trapping in air were: Tenax® TA 20/35 (Mandel Scientific), Carbotrap® B (Supelco), Carbosieve® S-111 (Supelco) and Bond Elut ENV (Varian Inc.). The main characteristics of the adsorbents evaluated in this study are briefly discussed below and the trap specifications summarised in Table A1 - 1 of Appendix 1.

**Tenax® TA** (TA) is a semi-crystalline porous polymer manufactured from 2,6-diphenyl-p-phenylene oxide (DPPO). It is one of the most commonly used adsorbent for MMHg measurement in water and sediment [98, 188, 189], due to its low background and relative thermal stability, which are desired characteristics when measuring trace concentrations. Tenax® TA has however low adsorption capacity due to its relatively small surface area (Table A1 - 1) and its use has been limited to high concentration measurements or analyte refocusing before analysis. Furthermore, highly volatile compounds are not always well retained on TA and its suitability for DMHg trapping is debatable.
Graphitized Carbon Black (GCB) materials are generally non-porous and highly pure products that have excellent thermal stability thus ensuring effective trapping and release by thermodesorption techniques. Carbotrap® B (CB), also known simply as Carbotrap®, has a higher surface area than TA and is effective in trapping volatile organics. CB is, however, less hydrophobic than TA and thus, more susceptible to moisture interferences. Carbotrap® B is used as an alternative to Tenax® TA when analysing MMHg [34, 190] or DMHg [30].

Carbon molecular sieve (CMS) is the micro-porous carbon skeletal framework remaining after the pyrolysis of a polymeric precursor. It has high surface area and adsorptive capacities, and thus, performs very well for trapping volatile analytes. CMS is also highly selective to very small molecular-sized compounds (C2 - C5) due to its closed-pore structures. However, the lack of tapered pores may result in larger analytes (> C5) blocking pores, preventing smaller ones from reaching available pore sites. CMS has also been reported to have substantially higher moisture trapping capacity than TA or even CB [191] and is therefore susceptible to moisture interferences. Carbosieve® SIII (CS), a common type of CMS, has been previously used for total Hg and DMHg [187] determination but no reports of CS for MMHg trapping has been found.

Styrene-divinylbenzene (SDVB) polymeric resins have been fairly recently developed (1990’s) and are being increasingly used for solid phase extraction (SPE) of a wide range of compounds from aqueous solutions [192, 193]. Bond Elut ENV (BE) and LiChrolut EN are commercially available and were shown to have much better performance than TA for gas-phase trapping of volatile organic compounds [194]. The applicability of (poly) styrene-divinylbenzene (e.g. Bond Elut ENV) has, to the best of our knowledge, not yet
been evaluated for gaseous organic Hg trapping and will be assessed for the first time in this study.

Analytical system

The adsorbents were evaluated first by measuring the recovery of MMHg and DMHg after loading. Subsequently, they were tested under situations comparable to field conditions when collecting these species from air i.e. flow rates ranging between 1 - 2 L min$^{-1}$, collection from large air volumes (100 – 200 L) and finally the stability and integrity of the trapped analytes during storage (weeks to months).

Collection traps

Collection traps were made by packing borosilicate tubes (11.5 cm long, 0.40 cm ID) with adsorbents as detailed in Table A1 - 1 (Appendix 1). Since BE is only available in small particle size (125 µm), wider tubes (0.7 cm ID) were used to minimize backpressure at a sampling flow rate of 1 L min$^{-1}$. Clean silanized glass wool was added at both ends of the tubes to retain the adsorbent firmly packed in the tube and prevent dragging during sampling and flushing (Figure 2 - 1). New adsorbent traps were conditioned by heating several times at 260 °C while flushing with Hg-free nitrogen (N$_2$) gas at a flow rate of 60-80 mL min$^{-1}$. Before each use, the traps were cleaned by heating three times, capped and stored in double bags in sealed glass jars until use.
Figure 2-1. Sampling and desorption directions (indicated by arrows) on solid adsorbent traps for collection of gaseous organic mercury species.

Reagents and Standards

The desired mass (50 - 250 pg) of MMHg and/or DMHg was loaded on individual traps by purging the analytical species from water onto the traps. MMHg (as methylmercurychloride) was converted to its volatile derivative methylethylmercury (MeEtHg), prior to purging by reaction with sodiumtetraethylborate (NaBEt₄, 1 % w/v) at pH 4.9 (adjusted with 2 M sodium acetate buffer) for 20 minutes in the sealed purging vessels. Since methylethylmercury (MeEtHg) is more volatile than methylmercurychloride and can be quantitatively purged from aqueous solution, it is commonly used as the analytical species in MMHg quantification [188, 190]. MMHg working standards were prepared daily from concentrated stock solutions of methylmercurychloride in 1 % nitric acid by dilution with MilliQ water. As for DMHg, no derivatization was required; known amounts were purged on the traps after careful injecting of appropriate volume of the stock solution (in methanol) in the purging vessels using a gastight syringe (Hamilton). A
sodalime trap followed by the collection trap was connected to the outlet of purging vessel and purging was performed at 60 mL min$^{-1}$ with Hg-free N$_2$ for 20 min. The purging set up used for preloading of the analytical species is illustrated in Figure 2 - 2.

To reduce the risks associated with manipulation of DMHg, optimization as well as preliminary adsorbent testing was done using MMHg, since its derivative, MeEtHg, is believed to have similar physical properties and behaviour as DMHg. Confirmatory tests with DMHg were conducted observing strict precautionary measures. **CAUTION:** Dimethylmercury is volatile and extremely toxic, causing neurological damage and death. Absorption by the skin and inhalation of the vapors must be avoided by vigilant handling under adequate ventilation and using proper personal protection equipment.

Isotopically enriched tracers (MM$^{201}$Hg and DM$^{198}$Hg) were also used during the preliminary tests to monitor potential degradation (conversion to Hg$^0$) during analysis and storage as well as for the breakthrough tests.
Figure 2-2. Schematic of the set up for (a) aqueous ethylation (for methylmercurychloride, MeHgCl) and precollection, (b) breakthrough volume determination and (c) thermodesorption for liberation of analytes (Methylethylmercury, MeEtHg and dimethylmercury, DMHg) from collection traps before quantification.
Analytical system

The method for the liberation and quantification of collected organic mercury species was adapted from a method described elsewhere [98]. The adsorbed analyte was liberated by thermodesorption and sent to a gas chromatography (GC) column for isothermal separation before detection by inductively coupled plasma mass spectrometry (ICP/MS). The ICP/MS instrument used was a Varian 820-MS (Varian, INC) while the GC column consisted of a silanized glass U tube packed with 15 % OV-3 on Chromasorb W-AW (DMCS, 80/100 mesh) and was maintained at 110 °C and 80 °C for MMHg and DMHg measurements, respectively, to ensure a good separation and thus peak identification during analysis. A desorption unit consisting of a nichrome heating coil connected to a variable transformer (Variac) was used to release the adsorbed analytes from the collection traps which were flushed directly to the GC column (i.e. no transfer to another analytical trap) using argon as the carrier gas at a flow rate of 30-40 mLmin⁻¹. The desorption temperature was set to 245 °C after optimisation, corresponding to the maximum temperature allowing complete recovery without any degradation of the Hg species. The air flow direction was reversed during thermodesorption, as shown in Figure 2–1, in order to maximise transfer of the released Hg species from the traps to the GC-ICP/MS.

Breakthrough volume

Breakthrough occurs when the target analyte travels along the adsorbent bed and eventually leaves the outlet of the collection trap as sampling volume increases. The maximum volume of air that can pass through the adsorbent without any significant loss of analyte is referred as the breakthrough volume. The breakthrough volume of the adsorbents evaluated was determined by quantifying the amount of preloaded analyte (MMHg and /
or DMHg) recovered after purging with increasing volume (2 - 100 L) of air. A backup trap was added at the outlet of the collection trap to collect and quantify any analyte not retained on the collection trap (% breakthrough). A gold trap and a sodalime moisture trap were put at the sampling inlet during purging to reduce possible interferences due to elevated elemental Hg concentration or moisture content in the incoming air.

Air was sucked through the analytical train by connecting a vacuum pump (Barnant Thermo Scientific 400-3910) to the end of the line. The flow rate was set to 1 Lmin\(^{-1}\) to ensure proper adsorption kinetics on the collection trap bed and no interference on breakthrough [195-197]. The exact volume of air was determined using a dry air meter (Actaris G1.6 Gallus 2000). A schematic of the set up used for breakthrough volume determination is shown in Figure 2 - 2 and detailed in Figure A1 - 1 (Appendix 1). The influence of temperature on the breakthrough volume was assessed at RT (~ 21°C) and 4°C.

**Storage**

The stability of MMHg and DMHg on the adsorbents was assessed by determining recovery after storage. Traps (in triplicates) were loaded with known amounts of MMHg and DMHg, capped on both ends with homemade Teflon plugs, wrapped in zipped bags and stored in air tight glass jars in the dark at 3 temperatures (~ 21 °C, 4 °C and -20 °C) and for periods ranging from a few days to a few months.

**Moisture interference**

Preliminary trials revealed a decrease in the adsorption efficiency of BE traps for organic Hg species with increasing moisture most probably as a result of competition and/or transformations in the water matrix of molecules adsorbed on BE particles. To the authors’
knowledge, it is the first time that the susceptibility of BE to moisture has been reported. This observation is, however, not surprising since reports of moisture interferences on adsorbents such as Carbotrap® B [30], Tenax GR and Carbosieve [191, 198, 199] have been reported in the past. The good behaviour of TA with increasing moisture was also confirmed during preliminary studies as the adsorption of TA was not affected with increasing moisture in the air stream.

To eliminate the risk of decreasing performance due to moisture, traps (PTFE, 10 cm long, ID 0.8 mm) packed with sodalime ACS (~2.5 g, 4-8 mesh, Alfa Aesar) were systematically added in front of adsorbent/collection traps to capture moisture. Sodalime was baked at 250 °C overnight to remove moisture and any Hg that might be present prior to packing. Traps were again baked at 110 °C after use to remove any accumulated moisture.

Furthermore, traps were dry-purged with Hg-free N₂ gas (50 mL min⁻¹ for 5 min) after loading to remove any humidity that might interfere with the stability of the analytes during storage. It has been demonstrated that most of the collected water is removed from carbon traps without any significant loss of analyte when purged with 30 to 300 mL of dry carrier gas [200].

**Statistical Analysis**

The % recoveries (mean ± SD) were calculated relative to the nominal mass of analyte added. Significant difference in % recoveries of the adsorbents was determined by performing a one-factor ANOVA followed by post hoc multiple comparisons using the Tukey test. The statistical significance was established with a p value of 0.05.
Results

Detection limits and precision

The precision of the MMHg determination using TA traps varied between 3 and 14 % RSD (relative standard deviation), while the calibration curves for determination of 0.5 to 250 pg of MMHg yielded linear correlations with both TA and BE traps ($r^2 = 0.992$ and 0.999, slope = 1.0012 and 0.987, intercept = 0.325 and 1.147 for TA and BE respectively). The limit of detection (LOD) defined as the amount of Hg required to yield a net peak that is 3 times the standard deviation of the ethylation blank (LOD = 3 x SD blank) was 0.15 pg while the limit of quantitation (LOQ) calculated as 10 times the standard deviation of the blank was 0.5 pg at 99% confidence interval. Details of the method detection limit and precision determination are given in Table A1 - 2 (Appendix 1). The preliminary trials and evaluation tests were done in triplicate and precision of RSD < 10 % were considered acceptable.

Trapping and Recovery

The chromatographic properties of DMHg and MMHg were not affected by the choice of adsorbent and retention times averaged $1.5 \pm 0.03$ (mean ± SD) and $3.0 \pm 0.50$ minutes, respectively. MMHg peaks with BE collection traps were similar to those obtained with TA analytical traps. MMHg peaks width averaged $2.2 \pm 0.278$ and $2.4 \pm 0.277$ minutes with BE and TA traps respectively.

The performance of adsorbents was determined by comparing the % recovery i.e. the amount of analyte recovered from the evaluated adsorbent relative to that of TA for MMHg and CB for DMHg, respectively, which are the most commonly used analytical traps for
quantification of these organic Hg species. The overall performance of the adsorbents tested for MMHg and DMHg trapping and recovery are presented in Figure 2 – 3.

Using TA and BE traps, MMHg showed quantitative average recoveries of 100 ± 8.1 % (n = 52) and 98 ± 9.2 % (n = 25), respectively. Statistical tests confirmed that there is no significant difference (p = 0.958) between the performance of BE and TA indicating that BE is as efficient as TA for MMHg trapping. CB and CS on the other hand showed low and variable recovery for MMHg. Only 61 ± 32.5 % (n = 72) of the analyte was recovered from CB traps while < 5% recovery was obtained with CS.

On the other hand, CB worked well for trapping DMHg showing excellent recoveries; 100 ± 0.3 % (n = 11). The lowest yield was obtained with CS traps, which recovered only 16 ± 2.8 % (n = 3) of DMHg. TA showed highly variable results for DMHg and overall, only 64 ± 17.3 % (n = 11) of DMHg was recovered. Interestingly, BE performed as well as CB for DMHg trapping with recoveries averaging 95 ± 8.1 % (n = 11). This was confirmed statistically since the performances of BE and CB (p = 0.99) were not significantly different.

Furthermore, BE was the only adsorbent that demonstrated very good homogeneity and repeatability (RSD < 10%) for both MMHg and DMHg.

Dual adsorbent traps were also investigated by mixing TA/CB and BE/CB at different proportions. CB/TA mixtures achieved quantitative MMHg and DMHg trapping and recovery at a ratio of roughly 1:3. The results for MMHg were however less reproducible as illustrated by the higher standard deviation in Figure 2 - 3.
Figure 2-3. Dimethylmercury (■ DMHg) and monomethylmercury (■ MMHg) recoveries (%, mean) with Tenax® TA - TA (0.1 g), Bond Elut ENV - BE (0.075 g), Carbotrap® B (0.4 g), Carbosieve® SIII – CS (0.5 g), CB/BE (Carbotrap® B / Bond Elut ENV – 0.35: 0.1 g) and CB/TA (Carbotrap® B / Tenax® TA - 0.15: 0.05 g) collection traps. Error bars indicate ± one standard deviation (n ≥ 3).
**Breakthrough Volume**

The breakthrough volume determination at 21°C and 4 °C for TA, BE and CB are presented in Figure 2 - 4. At 21 °C, significant ($p = 0.05$) loss was observed from TA traps when the sampling volume exceeded 15 L with up to $17 \pm 3.7\%$ of the MMHg recovered on the backup trap. For BE traps however, the first indications of breakthrough were observed when the sampling volume reached 40 L ($p < 0.05$).

As expected, the breakthrough volume for both adsorbents increased when subjected to lower temperature (4 °C) reaching up to 65 L for TA which is almost 4 times the breakthrough volume at higher temperature. No significant breakthrough was observed for BE at sampling volumes >100 L. The recovery after 200 L of air was still $91 \pm 6.1\%$ and statistically not significantly different from results obtained with 100 L ($p = 0.61$). No significant breakthrough was observed for DMHg on CB at 4 °C after sampling 100L of air ($99 \pm 0.3\%, p = 0.995$) while the recovery dropped to $62 \pm 9.0\%$, showing significant breakthrough, when the sampling volume reached 200L. More details of the breakthrough test results are given in Table A1 - 4 (Appendix 1).

Breakthrough of analyte from the main sampling trap onto subsequent traps was monitored for TA and is shown in Figure 2 - 5. At RT and a sampling volume of 15 L, breakthrough was observed and while up to $17 \pm 3.7\%$ of the loaded MMHg was transferred to the 1st backup trap, no transfer was observed on the 2nd backup trap. The influence of temperature on adsorption forces is clearly demonstrated by the slower transfer at lower temperature (4 °C) since the majority of the analyte (> 90%) was still retained on the collection trap at 40 L and no breakthrough observed on the 2nd backup trap. Breakthrough is observed on the 1st backup trap when the sampling volume reached 100 L, but complete recovery is obtained when combining the amount of MMHg collected on both
traps. However, as the sampling volume increased from 100 L to 120 L, the trapping efficiency of the collection trap decreased drastically (69 % to 35 %) and only 71 % of the loaded MMHg was obtained when summing up the recoveries of the collection and 3 backup traps in series.

Figure 2-4. Recovery (% mean) of monomethylmercury (MMHg) from Tenax® TA (TA, 4°C and 21 °C) and Bond Elut ENV (BE, 4°C and 21 °C) traps and dimethylmercury (DMHg) from Carbotrap® B (CB, 4°C) traps with increasing sampling volume.
Figure 2-5. The breakthrough of monomethylmercury (% recovery) on Tenax® TA traps in series, at (a) 4 °C and (b) 21 °C with increasing sampling volume.
**Storage Behavior**

*MMHg stability during storage at different temperatures*

The stability of MMHg (as methylethylHg) on TA during storage in the dark at different temperatures is presented in Figure 2 - 6. No significant degradation ($p > 0.05$) was observed after 3 weeks of storage at 4 °C and -20 °C showing recoveries of 97 ± 2.7 % and 106 ± 3.8 % respectively. However, significantly ($p < 0.05$) lower recovery (87 ± 0.6 %) was observed from the traps stored at RT indicating sample degradation or migration/evaporation during storage.

No significant difference in the stability of MMHg collected on either TA ($p = 0.26$) nor BE ($p = 0.95$) was observed when stored for longer periods (up to 120 days) at -20 °C in the dark (Figure 2 - 7). For CB traps however, a decrease of almost 50 % was noted in the amount of MMHg recovered (41 ± 25.6 % to 24 ± 6.4 %) after 90 days of storage suggesting that CB has not only low MMHg trapping efficiency but that any adsorbed MMHg is relatively unstable on CB.

*DMHg stability during storage*

DMHg seems to be less stable on the adsorbents considering that lower recoveries were recorded after storage (90 days at -20 °C in the dark) as shown in Figure 2 - 8. The most substantial drop in recovery (almost 25 %) was observed from CB traps with an average recovery of only 74 ± 1.4 %. Interestingly, DMHg demonstrated better stability on the other adsorbents as no significant ($p = 0.46$) decrease was observed from TA (66 ± 11.0 %) or BE traps. Even though TA has lower DMHg trapping efficiency than CB or BE, once collected, no statistically significant difference was observed when comparing TA to CB and BE. BE had again the best overall performance after DMHg trapping and storage since
even though a small (roughly 10%) decrease in recovery (95 ± 8.1% to 84 ± 19.2%) was observed after 90 days of storage, it was not statistically significant (p = 0.54).

Figure 2-6. Monomethylmercury (MMHg, as ethylmethylmercury) recovery (% mean) from Tenax® TA traps after 21 days of storage at varying temperatures. Error bars indicate ± one standard deviation (n ≥ 3).
Figure 2-7. Monomethylmercury (MMHg, as ethylmethylmercury) recovery (%, mean) from Tenax® TA (TA ▪), Bond Elut ENV (BE ▪) and Carbotrap® B (CB □) traps with storage time at -20°C in the dark. Error bars indicate ± one standard deviation (n ≥ 3).
Figure 2-8. Dimethylmercury (DMHg) recovery (% mean) from Tenax® TA (TA □), Bond Elut ENV (BE ■) and Carbotrap® B (CB ■) traps after 90 days of storage at -20 °C in the dark. Error bars indicate ± one standard deviation (n ≥ 3).
Discussion

Trapping and recovery

The results described above confirm the excellent performance of TA and CB for collecting MMHg (as MeEtHg) and DMHg respectively. They, however, also suggest that each of the two adsorbents has specific advantages. TA is less efficient at trapping DMHg while roughly only half of the spiked MMHg amount is recovered with CB after purging. No recovery values of DMHg from TA have been found in literature. However, the low breakthrough capacity of TA for collecting DMHg has been mentioned [30]. The lower trapping efficiency is presumably due to weaker binding forces between TA and DMHg molecules, thus allowing their easy liberation as sampling progresses, resulting in losses. On the other hand, the poor performance of CB is explained either by ethylmethylmercury molecules being too large to enter micropores, or the blockage of the pore entrance, thus preventing further adsorption and resulting in limited trapping.

As far as CS is concerned, and despite its very promising characteristics, barely any of the organic Hg loaded could be recovered. The very poor performance of CS might be due to poor thermodesorption behaviour, rather than low trapping efficiency since neither MMHg nor DMHg were ever found on backup traps during loading on CS traps. The desorption temperature (245 °C) was either too low or the desorption period was too short to allow liberation of the adsorbed Hg species. CS might, however, be appropriate if the proper desorption conditions are found and in situations where higher desorption temperatures can be used and separation of Hg species is not required. CMS adsorbent has been used for DMHg measurement [187] in the past by employing long desorption cycles and refocusing the desorbed DMHg on TA traps before quantification. However, losses of
DMHg during the refocusing step on TA cannot be ruled out (and should be accounted for) since TA, as reported earlier, may not trap DMHg quantitatively.

BE is evaluated for the first time as an adsorbent for volatile organic Hg preconcentration and showed the best overall performance. Both MMHg and DMHg were efficiently trapped and recovered, suggesting that BE may be an alternative to both TA and CB for MMHg and DMHg preconcentration during purge-and-trap from aqueous solutions. BE could also provide simultaneous trapping of both species on a single adsorbent which is not achieved quantitatively using TA or CB as discussed earlier. Furthermore, BE is a suitable analytical adsorbent providing excellent linear response over a wide mass range (5 – 250 pg), comparable to TA which is the most common analytical adsorbent for Hg species analysis involving GC.

**Breakthrough and the influence of temperature**

BE exhibited the best overall breakthrough performance, with collection volumes roughly three times higher than those achieved with TA before breakthrough occurred. The poor performance of TA was predictable since TA has a relatively low surface area. TA and BE breakthrough volumes substantially increased (from 15 L to > 65 L and 40 L to > 100 L for TA and BE respectively) when the sampling temperature was lowered from 21°C to 4°C demonstrating the effect of temperature on trapping efficiency of adsorbents.

Another reliable option to increase the sampling volume and quantitatively collect organic Hg is the use of multiple traps in series to collect any eluting analyte and adding up the recovered amounts on each trap to determine the overall mass of analyte adsorbed. This is particularly applicable to TA since the traps showed very good reproducibility and there was no degradation or loss of the analyte during transfer to the analytical trap. No
significant loss was observed when cumulating the recoveries of the collection trap and back up trap at 15L (at 21°C) while at 4 °C, up to 100L of air could be sampled without any loss when adding 3 TA traps in series. However, the collection trap showed a sudden decrease in trapping efficiency with increasing volume (> 100 L) due to either saturation of the adsorbent bed or displacement of the analyte of interest by other compounds. This suggests that the sampling volume can be increased up to a certain volume above which the recoveries are less predictable.

Since minor changes in sampling conditions and the presence of other compounds (e.g. VOC’s for CB) in sample air can affect the trapping efficiency and breakthrough volume of adsorbents, it is advisable to use a safe sampling volume (SSV), usually set at two-thirds of the breakthrough volume [201, 202], to account for possible decrease in performance, especially under field conditions. From the results obtained, the SSV, at 21°C would be 10L and 30L for TA and BE respectively while at 4°C, the SSV would be 40 L, 130 L and 80 L for TA, BE and CB respectively (Table 2 - 1).

It should be noted, however, that these recommendations are rather conservative since the concentrations under field conditions are expected to be much lower than the one used for breakthrough volume determination and would not be loaded at once but rather preconcentrate as sampling progresses. A schematic for preconcentration of MMHg and DMHg from air is given in Figure A1 - 2 (Supplementary document).

**Stability of organic Hg during storage**

MMHg and DMHg showed very good stability on TA and BE while degradation was observed on CB after three months of storage. The instability of DMHg on CB during storage is most probably explained by interferences due to remaining moisture despite the
use of moisture traps and dry purging after sampling. The effect of moisture on the stability of DMHg on CB has been suggested in a previous study [30] with improved stability when purged with dry argon before storage. The volume of air (1000 - 2000 mL) used for drying was higher than the one used in this study (250 – 300 mL) which may explain why the stability results were less favorable for CB in this study. The results presented here demonstrate the worst case scenario since under real sampling conditions the % relative humidity (RH) should be lower than during DMHg loading with the purge and trap method. Furthermore, when “cold” sampling is performed, most of the water is removed by condensation due to the lower temperature (4°C) of the sampling line, before the air stream reaches the collection trap. It is thus safe to say that the conditions under which the stability was tested amplified moisture interferences potential. The stability of DMHg on CB should be much better under real sampling conditions and for durations shorter than 3 months.

**Suitability of BE, TA and CB for DMHg and MMHg trapping**

The good performance of TA and CB for trapping MMHg and DMHg respectively, confirms their suitability as reference adsorbents. However, this evaluation also suggests that contrary to the general consensus, TA and CB cannot be interchanged or presented as alternatives to each other since doing so would lead to underestimation of one of the organic Hg species.

Mixing the adsorbents (e.g. CB and TA or CB and BE) can meet specific needs such as simultaneous trapping of MMHg and DMHg or increasing the breakthrough volume. However, the various characteristics and limitations of the “dual adsorbent” traps have to be extensively tested prior to use as the performance of the dual adsorbent will not only
depend on the individual characteristics of the adsorbents but also the combined effect of the mixed adsorbent. This is illustrated in this study showing lower recovery for MMHg on the CB/BE trap compared to BE traps alone. The poorer performance is most probably due to the fact that both CB and BE are slightly hydrophilic resulting in more moisture being trapped and thus affecting MMHg (as methylethylHg) adsorption. The trapping efficiency was however improved by the CB/TA dual trap allowing the simultaneous trapping of MMHg and DMHg which was not achieved by the individual adsorbents. Preliminary tests and proper optimization under actual sampling conditions (e.g. sampling flow rate, duration and temperature) are however imperative to determine the appropriate mixing ratio so that there is acceptable trapping and recovery and no significant breakthrough of either species.

Overall, BE appears to be the most suitable adsorbent in collection traps as well as analytical traps. BE not only performs very well during sampling allowing quantitative recovery and preservation of sample integrity over months of storage but also offers chromatographic properties comparable to TA. BE is thus a very interesting alternative to both TA and CB for the collection of volatile organic Hg species using purge-and-trap methods while allowing more versatility and flexibility since BE traps could be interchangeably used for trapping either MMHg or DMHg or both. BE also appears as a very promising adsorbent for preconcentration of ultra-trace levels of MMHg and DMHg from large air and water samples with the opportunity for prolonged storage as might be the case in long or remote sampling campaigns.

The only note of caution for BE is its susceptibility to moisture that could greatly affect the performance under high moisture conditions. The use of a proper drying agent (e.g. sodalime) to trap moisture in the sample line, and appropriate dry purging (with N₂) after
sampling, should alleviate this problem. Based on the evaluation results, the suitability of
the adsorbents for different air sampling conditions are summarized in Table 2 - 1.
Table 2-1 Recommended set up and conditions for the sampling of gaseous organic mercury species by online solid phase adsorption on collection traps.

<table>
<thead>
<tr>
<th></th>
<th>Tenax® TA</th>
<th>Bond Elut ENV</th>
<th>Carbotrap® B</th>
<th>Mixture CB / TA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>2,6-diphenyl-p-phenylene oxide</td>
<td>styrene-divinylbenzene</td>
<td>Graphitized Carbon Black</td>
<td>Carbotrap® B / Tenax® TA /</td>
</tr>
<tr>
<td>Amount (g)</td>
<td>0.1</td>
<td>0.1</td>
<td>0.4</td>
<td>0.15 / 0.05</td>
</tr>
<tr>
<td>Breakthrough Volume (L)</td>
<td>15</td>
<td>40</td>
<td>40</td>
<td>15</td>
</tr>
<tr>
<td>at 21 °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sampling Volume (L)</td>
<td>10</td>
<td>30</td>
<td>30</td>
<td>10</td>
</tr>
<tr>
<td>at 21 °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Breakthrough Volume (L)</td>
<td>65</td>
<td>150</td>
<td>150</td>
<td>65</td>
</tr>
<tr>
<td>at 4 °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sampling Volume (L)</td>
<td>40</td>
<td>100</td>
<td>100</td>
<td>40</td>
</tr>
<tr>
<td>at 4 °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Max. Storage Duration</td>
<td>1 month</td>
<td>1 month</td>
<td>1 month</td>
<td>1 month</td>
</tr>
<tr>
<td>at 4 °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Max. Storage Duration</td>
<td>4 months</td>
<td>4 months</td>
<td>2 months</td>
<td>2 months</td>
</tr>
<tr>
<td>at -20 °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Analyte</td>
<td>MMHg</td>
<td>MMHg &amp; DMHg</td>
<td>DMHg</td>
<td>MMHg &amp; DMHg</td>
</tr>
</tbody>
</table>

Data are relevant for sampling flow rate between 1-1.5 Lmin⁻¹, use of a sodalime moisture trap at sampling inlet and maximum analyte concentration below 250 pgL⁻¹

MMHg - Monomethylmercury, DMHg - Dimethylmercury
Conclusions

It has been shown that with the exception of CS, the adsorbents evaluated can be adapted to the sampling of MMHg or DMHg or both. However, the choice and suitability of the adsorbent or adsorbent mixture is dictated by the sampling conditions and need.

TA and CB are suitable adsorbents for trapping one analyte at a time (TA for MMHg and CB for DMHg) and should not be interchanged to avoid erroneous results. Furthermore, the above adsorbents are recommended for sampling smaller air volumes at higher concentrations and for a relatively short storage period due to the low breakthrough volume and instability of DMHg on CB.

Bond Elut ENV, which is evaluated here for the first time, offers more versatility and flexibility as it performs very well for the preconcentration of both MMHg and DMHg from large sampling volumes and provides longer storage periods. It is thus a reliable alternative to both Tenax® TA and Carbotrap® B for volatile organic Hg trapping from aqueous solutions, especially in cases where extended purging is required or delayed analysis cannot be avoided. Most importantly, Bond Elut ENV offers new opportunities as it has the desired adsorbent characteristics needed for collection traps used for the simultaneous sampling and quantification of MMHg and DMHg in air.

Supplementary Information

Supplementary data associated with this article can be found, in Appendix 1.
Literature Cited


53. Woolfenden, E.A., McClenny, W. A., Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air TO-17: Determination
CHAPTER 3: DETERMINATION OF MONOMETHYLMERCURY AND DIMETHYLMERCURY IN THE ARCTIC MARINE BOUNDARY LAYER
Abstract

Our understanding of the biogeochemical cycling of monomethylmercury (MMHg) in the Arctic is incomplete because atmospheric sources and sinks of MMHg are still unclear. We sampled air in the Canadian Arctic marine boundary layer to quantify, for the first time, atmospheric concentrations of methylated Hg species (both MMHg and dimethylmercury (DMHg)), and, estimate the importance of atmospheric deposition as a source of MMHg to Arctic land- and sea-scapes. Atmospheric MMHg and DMHg concentrations were 2.9 ± 3.6 (mean ± SD) and 3.8 ± 3.1 pg m⁻³, respectively. Concentrations of methylated Hg species in the marine boundary layer significantly varied amongst our sites, with a predominance of MMHg over Hudson Bay (HB), and DMHg over Canadian Arctic Archipelago (CAA) waters. We concluded that DMHg is of marine origin and that primary production rate and sea-ice cover are major drivers of its concentration in the marine boundary layer. Summer wet deposition rates of atmospheric MMHg, likely to be the product of DMHg degradation in the atmosphere, were estimated at 188 ± 117.5 ng m⁻² and 37 ± 21.7 ng m⁻² for HB and CAA, respectively, sustaining MMHg concentrations available for bio-magnification in the pelagic food web.

Keywords: Monomethylmercury, dimethylmercury, atmosphere, Arctic, ocean
**Introduction**

Gaseous elemental mercury (Hg⁰) has a long atmospheric residence time (~ 6 – 12 months), and can therefore be transported long distances from natural or anthropogenic sources to remote and pristine areas. However, once oxidized to reactive mercury (Hg²⁺), it is rapidly deposited to surfaces. Globally, atmospheric deposition of Hg²⁺ is the major source of Hg to marine ecosystems [1-3]. This is even more relevant to the Arctic Ocean, where there are virtually no local anthropogenic sources of Hg. Furthermore, atmospheric Hg depletion events (AMDEs), a springtime phenomenon unique to polar regions, may deposit reactive and particulate-bound Hg to open water regions [4] contributing to the pool of oxidized Hg available for methylation. Once Hg²⁺ reaches marine waters, it may be methylated to monomethylmercury (MMHg) and dimethylmercury (DMHg) [5, 6]. From a human health perspective, MMHg is the most toxic and bio-accumulative form of Hg and constitutes the majority (> 80%) of Hg present in marine animals [7]. Elevated Hg concentrations currently found in Arctic marine mammals and fishes [7, 8] represents a health threat to local populations, whose traditional country diet is mainly marine derived.

Unfortunately our understanding of Arctic marine Hg biogeochemistry remains incomplete despite numerous studies over the past decades e.g., [5, 9-11].

The source of MMHg in open waters is believed to be mainly from *in situ* methylation of Hg²⁺ in surface oxic water and subsurface regions of the water column, where organic matter remineralization also occurs [5, 6, 11-14]. Atmospheric deposition of MMHg is an additional, and potentially important, source of MMHg but has yet to be properly quantified. Atmospheric contribution of MMHg to surface water has been postulated following numerous reports of MMHg in oceanic precipitation [15, 16] or in Arctic snow.
The origin of MMHg in the atmosphere and precipitation is still unclear, but hypotheses put forth include (i) aqueous atmospheric Hg methylation in the presence of acetate [15, 18], (ii) the evasion of MMHg (mainly the chloride complex, CH$_3$HgCl) from surfaces [19, 20] and finally (iii) the degradation of DMHg to MMHg in the atmosphere [9, 21] following its evasion from surface marine waters.

Unfortunately, these hypotheses are very difficult to test. There are very few measurements of methylated Hg (both MMHg and DMHg) species in air [22-25] mainly due to the analytical challenges and sampling constraints posed by the suspected trace concentrations. However, using a newly developed sampling method based on solid phase adsorption [26], we investigated the presence of methylated Hg species in the Arctic marine boundary layer (MBL). Two sampling campaigns were conducted in the Canadian Arctic in summer 2010 and 2011. We document here for the first time the presence of both MMHg and DMHg in the Arctic MBL and discuss parameters potentially controlling the concentrations of these species in air.
Methods

Study site

Sampling was conducted in the Canadian high and sub Arctic (56°27’ to 74°43’N; 62°42’ to 110°48’W) onboard the Canadian research icebreaker CCGS *Amundsen* during ArcticNet (http://www.arcticnet.ulaval.ca/) expeditions (Figure 3 - 1). To assess the spatial distribution of methylated Hg species, from 19 July to 10 August 2010, air and water samples were collected from southwestern Hudson Bay (HB), and through the Northwest Passage in the Canadian Arctic Archipelago (CAA), via Lancaster Sound, Barrow Strait, Peel Sound, Franklin Strait, Queen Maud Gulf and Coronation Gulf. Another sampling campaign took place the following year (31 July to 10 August 2011) in the CAA to investigate temporal trends in methylated Hg species. The 2010 and 2011 ship cruise tracks, as well as air sampling locations, are shown in Figure 3 - 1. A description of the study area is given in Appendix 2.
Figure 3-1. Map of the study area showing the cruise tracks and air sampling locations for methylated Hg species (monomethylmercury and dimethylmercury) determination in 2010 (○) and 2011 (●). See Table 3-1 for site characteristics.
**Air sampling**

The main steps for the determination of gaseous MMHg and DMHg involve active sampling, online ethylation, *in situ* preconcentration and quantification in the laboratory.

**Active sampling**

Sampling involved the pumping of approximately 200 L of air from above the sea surface through insulated PTFE tubing (10 m long, Cole-Parmer®) to the sampling unit at a rate of 1 L min⁻¹ using a vacuum pump (Barnant Thermo Scientific 400-3910). A particulate filter (≤ 0.45 µm) was added at the beginning of the sampling line to remove particles and sea salt aerosols. The pump was started a few hours before sampling to ensure constant air flow in, and sufficient flushing of, the sampling line. The sampling inlet was set up at the bow of the ship ~ 7 m above the sea surface. Sampling was conducted during ship transit (22 to 27 km hr⁻¹) under headwind conditions (wind direction of 60E and 60W relative to direction of travel) and moderate absolute wind speed (≤ 10 m s⁻¹) to minimize interferences and contamination from the ship.

**Online ethylation and preconcentration**

Derivatization of MMHg species (presumably consisting mainly of CH₃HgCl and CH₃HgBr) [27] to volatile ethylmethylmercury allows efficient collection and recovery of MMHg species on the solid adsorbent traps, whereas no derivatization was required for DMHg collection. Online ethylation, adapted from Larsson et al. (2005) [28], consisted of passing the air stream through an ethylation filter (0.45 µm cellulose filter) presoaked with ethylating reagent (sodiumtetraethylborate - NaBE₄, 1% w/v at pH 4.9 adjusted with 2 M sodium acetate buffer) for the derivatization of MMHg to volatile ethylmethylmercury. The air stream was dried through a sodalime trap (4 – 8 mesh sodalime ACS, Alfa Aesar) and
passed through collections traps (borosilicate glass tubes packed with either Tenax® TA 20/35, Mandel Scientific or Bond Elut ENV Varian Inc.) for preconcentration of MMHg and DMHg. Detailed procedures are described in the Supplementary Information.

**Measurement in the laboratory**

The measurement of the collected methylated Hg species involved release from the traps by thermodesorption followed by gas chromatographic (GC) separation and quantification by inductively coupled plasma mass spectrometry (ICPMS) [26, 29]. Air samples were stored in air tight glass containers, backfilled with UHP nitrogen gas, at -20°C in the dark and analyzed within two months of sampling.

A schematic of the sampling set up is presented in Figure A2 - 1, and the analytical steps, as well as collection traps characteristics and performances for methylated Hg species, are detailed in a previous paper [26].

Preliminary tests in the laboratory with the sample system yielded online ethylation recoveries of 89 ± 17.2%. The limit of quantification (LOQ) calculated as ten times the standard deviation of bubbler blank (10 SD<sub>bubbler blank</sub>) used for standards, was 0.5 pg whereas the limit of detection (LOD, 3 SD<sub>bubbler blank</sub>) was 0.15 pg. Processing of 1 pg standards of MMHg yielded a signal response which was significantly larger than the calculated LOQ.

Concentrations of both MMHg and DMHg were below the LOD for the travel blanks, while no significant loss of MMHg or DMHg (t-test, \( p < 0.001 \)) was observed from the standard traps, during the storage period of three months.
**Water sampling**

In addition to measurements in air, seawater was also collected for the determination of MMHg and DMHg concentrations in HB in 2010 and in CAA in 2010 and 2011. Water samples at the surface (2 – 5 m) and at the depth of the subsurface chlorophyll maximum (SCM) were collected with a carousel water sampler (Sea-Bird 32, Sea-Bird Electronics, Inc.) equipped with 12 L Teflon® lined Niskin-type bottles (General Oceanics), following strict protocols for trace metal sampling [30, 31]. Water samples were collected at one location along each air sampling route (which extended 50 to 70 km from the air sample start location). Water samples were decanted into acid cleaned glass bottles and stored at -20°C until analysis (within 8 months) by isotope dilution distillation, aqueous phase ethylation and determination by GC-ICP/MS [32].

**Ancillary data and calculations**

Vertical profiles of oceanographic variables such as temperature, salinity, dissolved oxygen and *in vivo* fluorescence were measured appropriate sensors. Water samples were collected for dissolved organic carbon (DOC), which is known to influence Hg bioavailability and methylation, at a minimum of 4 depths in the upper 100 m of the water column. Chlorophyll *a* concentration and net primary production (PP) rates were measured at 7 optical depths (i.e., 100, 50, 30, 15, 5, 1, and 0.2% of surface irradiance) in the water column. Details for the measurement of ancillary parameters are provided in the Supplementary Information. Atmospheric variables known to influence gas exchange across the seawater-air interface and photochemical reactions of Hg, such as air temperature, wind speed and incident downwelling photosynthetically available radiation (PAR, 400-700 nm) were also measured during air sampling as described elsewhere [33].
Daily sea-ice concentrations were estimated from satellite imagery (F17 special sensor microwave imager (SSMI/S); ~ 25 km spatial resolution) obtained from the F17 special sensor microwave imager (SSMI/S) by the National Snow and Ice Data Center (NSIDC) [34].
Results

**Biogeochemical characteristics of study area**

The water column depths at sampling locations ranged from 35 m to 120 m in HB and from 80 m in Queen Maud Gulf to 725 m at the eastern entrance of Lancaster Sound in the CAA (Table A2 - 1). Average depths of the surface mixed layer (12 ± 7 m) and of the subsurface chlorophyll maximum (SCM, 29 ±11 m) were roughly the same in both regions. Higher mean incident PAR was observed in HB while PP was higher in the CAA (Table 3 - 1). However, these noticeable differences were not statistically significant. The most significant differences between the two regions were higher air and seawater temperatures and seawater DOC concentrations in HB and significantly higher % ice and cloud cover in CAA (Table 3 - 1). Even though HB is completely covered with sea-ice at the end of winter, HB was ice-free during our sampling period (19 to 31 July). In the CAA, average sea-ice cover during our sampling period (31 July to 10 August) was higher (17%) in 2010 than in 2011 (5%) due to an earlier onset of ice melting in 2011. Lancaster Sound had roughly 15% ice cover during the sampling period in 2010 while it was ice free in 2011. The regions with most ice cover were Franklin Strait and Queen Maud Gulf with 40% and 23% ice cover during the sampling periods in 2010 and 2011, respectively (Figure A2 - 3). The different sea conditions encountered during sampling campaigns are shown in Figure A2 - 2 and other environmental characteristics of the HB and CAA regions are given in Table 3 - 1.
Table 3-1. Average (Mean ± SD) environmental and biological variables in Hudson Bay (HB) and Canadian Arctic Archipelago (CAA) during air sampling period (July - August 2010 and 2011).

<table>
<thead>
<tr>
<th>Variable</th>
<th>HB 2010</th>
<th>CAA 2010</th>
<th>CAA 2011</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air temperature (°C)</td>
<td>9 ± 4.5 *</td>
<td>4 ± 2.9</td>
<td>6 ± 2.7</td>
</tr>
<tr>
<td>Relative Humidity (%)</td>
<td>96 ± 6.1</td>
<td>93 ± 4.4</td>
<td>92 ± 5.4</td>
</tr>
<tr>
<td>Sea surface temperature (°C)</td>
<td>5 ± 2.8 **</td>
<td>3 ± 2.5</td>
<td>3 ± 1.2</td>
</tr>
<tr>
<td>Sea surface salinity (psu)</td>
<td>28 ± 1.8</td>
<td>28 ± 1.8</td>
<td>26 ± 4.5</td>
</tr>
<tr>
<td>PAR (µmol photons m⁻² s⁻¹) a</td>
<td>446 ± 539</td>
<td>381 ± 450</td>
<td>375 ± 367</td>
</tr>
<tr>
<td>Wind speed (m s⁻¹) a</td>
<td>3.4 ± 1.44</td>
<td>3.6 ± 0.92</td>
<td>3.4 ± 1.42</td>
</tr>
<tr>
<td>Ice cover (%) b</td>
<td>0 *</td>
<td>17 ± 9</td>
<td>5 ± 6</td>
</tr>
<tr>
<td>Cloud cover (%) b</td>
<td>30 ± 26 **</td>
<td>70 ± 20</td>
<td>66 ± 27</td>
</tr>
<tr>
<td>Water column depth (m)</td>
<td>82 ± 51</td>
<td>269 ± 234</td>
<td>222 ± 197</td>
</tr>
<tr>
<td>Mixed layer depth (m)</td>
<td>12 ± 6</td>
<td>10 ± 5</td>
<td>11 ± 7.5</td>
</tr>
<tr>
<td>SCM depth (m) c</td>
<td>30 ± 10</td>
<td>27 ± 5</td>
<td>29 ± 14</td>
</tr>
<tr>
<td>DOC (µmol L⁻¹) d</td>
<td>104 ± 12.8(10) ***</td>
<td>72 ± 3.9 (5)</td>
<td>69 ± 3.5 (8)</td>
</tr>
<tr>
<td>PP (mg C m⁻² d⁻¹) e</td>
<td>395 ± 265 (6)</td>
<td>1072 ± 711 (4)</td>
<td>734 ± 663 (7)</td>
</tr>
</tbody>
</table>

a Wind speed and incident downwelling PAR (photosynthetically available radiation) are given as daily average for sample day.

b % Ice cover and cloud cover derived from satellite data (F17 special sensor microwave imager -SSMI/S) from the National Snow and Ice Data Center (NSIDC).

c SCM - subsurface chlorophyll maximum.

d DOC – Dissolved organic carbon, integrated over 100 m or bottom depth if shallower and divided by the integration depth.

e PP – Primary production calculated using trapezoidal integration over the euphotic zone (i.e depth receiving 0.2 % surface PAR).

DOC and PP were not determined at all the stations and the sample size is given in parenthesis, (n).

p is the level of significance of the difference between HB, CAA 2010 and CAA 2011. p was assessed using an analysis of variance (ANOVA).

* p ≤ 0.05, ** p ≤ 0.01, *** p ≤ 0.001.
Methylated Hg concentrations in air

Methylated Hg species were detected in the Arctic MBL at low concentrations. MMHg concentrations ranged from < 0.5 (LOQ) to 12.7 pg m\(^{-3}\), whereas DMHg concentrations ranged from < 0.5 to 11.3 pg m\(^{-3}\) (Figure 3 - 2). MMHg concentrations were below the LOQ (< 0.5 pg m\(^{-3}\)) during 16 of the 37 sampling events and these non-detect events occurred mainly in 2011 in the CAA. Since we prefILTERED air before the collection trap, we only measured gaseous MMHg. We would therefore expect higher concentrations of MMHg if we also included MMHg bound to particulate and sea-salt aerosols in our samples. DMHg concentrations were < LOQ during 4 sampling events only (Table A2 - 1). Samples that were below LOD were assigned a concentration of 0.25 pg m\(^{-3}\), which is equal to half the LOQ, for statistical purposes.

Concentrations of MMHg and DMHg in the MBL varied significantly amongst the sites (Figure 3 - 1b and Table 3 - 2). For example, MMHg concentrations were significantly (t-test, \(p \leq 0.01\)) higher over HB (7.5 ± 4.7 pg m\(^{-3}\)) than over the CAA (3.6 ± 2.1 pg m\(^{-3}\) and 0.8 ± 1.7 pg m\(^{-3}\) for 2010 and 2011, respectively) whereas DMHg concentrations were significantly (t-test, \(p \leq 0.01\)) higher over the CAA (5.4 ± 2.9 pg m\(^{-3}\) and 3.7 ± 3.2 pg m\(^{-3}\) for 2010 and 2011, respectively) than over HB (1.3 ± 1.2 pg m\(^{-3}\)). There were differences in the dominant methylated Hg species occurring in the MBL of each region. Over HB, concentrations of MMHg were higher than DMHg whereas over the CAA, DMHg was more abundant than MMHg (t-test, \(p \leq 0.01\) in all cases).

Overall, mean (± 1 SD) MMHg and DMHg concentrations in the Arctic MBL at all sites were 2.9 ± 3.6 (\(n = 37\)) and 3.7 ± 3.1 (\(n = 37\)) pg m\(^{-3}\), respectively. MMHg concentrations were, on average, significantly higher (t-test, \(p < 0.001\)) in 2010 compared to 2011 (Figure 3 - 2 and Table 3 - 2) due to the elevated concentrations recorded in the HB MBL.
sampled in 2010 only. Average DMHg concentrations in the MBL did not differ between the two years.

A previous study measuring methylated Hg species in polar air reported much higher MMHg concentrations (range: 5 to 97 pg m\(^{-3}\)) but comparable DMHg concentrations (up to 14 pg m\(^{-3}\)) [25]. The concentrations of methylated Hg species reported here are also comparable to those reported in urban air (0.5 to 22 pg m\(^{-3}\)) [22, 23].

Even though methylated Hg species represent only a minor (~ 1%) fraction of the total atmospheric gaseous Hg pool, our results suggest that MMHg may constitute up to 25% of reactive gaseous mercury (RGM; mean 30.1 pg m\(^{-3}\), range 3.5 – 105.4 pg m\(^{-3}\)) over Arctic sea ice [35].
Figure 3-2. Spatial distribution of (a) monomethylmercury (MMHg) and (b) dimethylmercury (DMHg), in pg m$^{-3}$, in Hudson Bay and the Canadian Arctic Archipelago marine boundary layer in summer (mid-July to mid-August).
Table 3-2. Monomethylmercury (MMHg) and dimethylmercury (DMHg) average concentrations in the Arctic marine boundary layer (pg m$^{-3}$) and in the water column (pg L$^{-1}$) in Hudson Bay (HB) and the Canadian Arctic Archipelago (CAA) for summer (July to August) 2010 and 2011. Errors represent one SD.

<table>
<thead>
<tr>
<th></th>
<th>2010</th>
<th>2011</th>
<th>2010</th>
<th>2011</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>MMHg</td>
<td>DMHg</td>
<td>MMHg</td>
<td>DMHg</td>
</tr>
<tr>
<td>Air</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HB</td>
<td>7.5 ± 4.7</td>
<td>1.3 ± 1.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CAA</td>
<td>3.6 ± 2.1</td>
<td>5.4 ± 2.9</td>
<td>0.8 ± 1.7</td>
<td>3.7 ± 3.2</td>
</tr>
<tr>
<td>Seawater surface</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HB</td>
<td>15.3 ± 6.96</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CAA</td>
<td>17.6 ± 5.16</td>
<td>6.8 ± 6.0</td>
<td>25.7 ± 26.43</td>
<td>3.4 ± 1.96</td>
</tr>
<tr>
<td>Subsurface Chlorophyll maximum (SCM)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HB</td>
<td>20.9 ± 18.46</td>
<td>5.6 ± 4.12</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CAA</td>
<td>16.7 ± 2.05</td>
<td>24.3 ± 5.02</td>
<td>20.1 ± 11.35</td>
<td>13.0 ± 7.98</td>
</tr>
<tr>
<td>Bottom</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HB</td>
<td>35.0 ± 22.12</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CAA</td>
<td>27.2 ± 18.9</td>
<td>31.0 ± 10.52</td>
<td>38.8 ± 35.67</td>
<td>-</td>
</tr>
</tbody>
</table>

A value of 0.25 pg m$^{-3}$ (0.5 x LOQ) was assigned to air samples with concentrations less than the limit of detection. See Table A2 – 1.
**Methylated Hg species in seawater**

The presence of methylated Hg species in the MBL is expected to be influenced by seawater-air interactions such as gas evasion and deposition. This was investigated by measuring the concentrations of both MMHg and DMHg in water at the MBL sampling locations. Concentrations of methylated Hg species in the water column reported here (see Table 3 - 2) are consistent with previously reported values for Arctic marine waters [5, 9, 10], as well as for Pacific [36], Equatorial Pacific [21], Northern Atlantic [37] and Mediterranean [38] waters.

Although significantly lower concentrations of MMHg were observed in the CAA MBL than over HB, concentrations of MMHg in the water column (SCM ~ 30 m) in HB (20.9 ± 18.46 pg L⁻¹) were not significantly different than those in the CAA (16.7 ± 2.05 and 20.1 ± 11.35 pg L⁻¹ for 2010 and 2011, respectively) (Table 3 - 2). Concentrations of DMHg in the water column of the CAA (24.3 ± 5.02 pg L⁻¹ and 13.0 ± 8.0 pg L⁻¹ for 2010 and 2011, respectively), however, were significantly higher ($t$-test, $p \leq 0.001$) than in HB (5.6 ± 4.12 pg L⁻¹) consistent with observations in the MBL (Figure 3 - 3b, d). Higher DMHg concentrations in both the MBL and waters of the CAA region relative to HB, may suggest that environmental conditions in the CAA are either conducive to DMHg formation or that DMHg is more stable and more persistent there, or both.

At the SCM, MMHg was the predominant methylated Hg species in HB waters, (MMHg:DMHg = 4), which was similar to observations made for air, although the ratio of MMHg was higher in air (MMHg:DMHg = 10). In the CAA however, the proportion of methylated Hg species was roughly the same in the MBL and at the SCM in the water column (MMHg:DMHg < 1).
The mirrored trend in the proportion of methylated Hg species in the MBL and water suggests that the two pools are closely interconnected through gas evasion and deposition at the seawater-air interface. Changes in one compartment might easily affect concentrations in the other. However, from our study it is difficult to conclude if one compartment is the main driver of the other, or if we are dealing with an intricately linked feedback loop.

The higher MMHg:DMHg ratio in the MBL (10) compared to water at the SCM (4) in HB suggests that MMHg is produced in the air, likely as the result of the photochemical decomposition of DMHg (see also section 3.4). If this hypothesis was correct it should result in the deposition of MMHg to surface waters. However, no enrichment in surface water MMHg concentrations was observed, at least relative to MMHg concentrations in the SCM. Low concentrations of MMHg in surface waters could be due to enhanced photodemethylation there, regardless of whether MMHg comes from the atmosphere or in-situ production. Water column profiles (Table 3 - 2) show a depletion of DMHg at the surface. This is presumably a result of evasion to the atmosphere and suggests that marine waters are a source of atmospheric DMHg. The lower MMHg:DMHg ratio in the CAA MBL also suggests that different and most probably, site specific parameters, such as the presence of sea ice, were influencing methylated Hg species in these two areas. The influence of meteorological and oceanographic variables will be explored below to identify the possible processes controlling the presence and biogeochemical cycling of these methylated Hg species in the marine boundary layer.
Figure 3-3. Monomethylmercury (MMHg) and dimethylmercury (DMHg) concentrations in the Arctic marine boundary layer (a) averaged for 2010 and 2011 and (b) for Hudson Bay (HB) and the Canadian Arctic Archipelago (CAA). Methylated air concentrations in 2010 are from HB and CAA while those for 2011 are from CAA solely. Concentrations of (c) MMHg in the water column at the surface, subsurface chlorophyll maximum (SCM) and bottom depths and of (d) MMHg and DMHg at the SCM (depth ~ 30 m). In (a) and (c), the error bars represent one standard deviation. In (b) and (d), boxes extend from 25 to 75 % quartiles with the middle line representing the median value; the whiskers extend from minimum to maximum values.
**DMHg and MMHg interactions in air**

Since both DMHg and some volatile complexes of MMHg (e.g., CH₃HgCl [20]) can evade from ocean surfaces, we hypothesize that methylated Hg species present in the Arctic MBL are mainly of marine origin. However, we suspect a greater contribution of marine derived DMHg to the atmosphere as it has lower solubility in seawater and much higher volatility (gas-aqueous distribution constant, H = 0.31) [39] than MMHg chloride complexes (H = 1.9 x 10⁻⁵) [40]. Once in the atmosphere, DMHg is unstable and is expected to degrade rapidly to MMHg in the presence of light and oxidants such as OH radicals [41] and chlorine atoms [42]. The degradation of DMHg in the atmosphere would thus contribute to the pool of MMHg in the MBL, which in turn would be deposited fairly rapidly to ocean surfaces. It has been suggested that the DMHg residence time in the atmosphere is less than one day, and as such, high DMHg concentrations should be recorded close to its sources only [43].

**Sources of DMHg in the MBL**

High concentrations of both MMHg and DMHg were recorded at some locations in the CAA MBL (i.e., at stations in western Lancaster Sound, Franklin Strait and from Coronation Gulf, Figure 3 - 2). It is noteworthy that sea ice was still present at the time of sampling (roughly 30 %, Figure A2 - 2-S4). Sea ice cover is known to reduce ocean–atmosphere exchange, as well as limit the photodegradation of methylated Hg species in the underlying surface water because ultraviolet radiation is attenuated as it passes through snow and sea ice [44, 45]. The strong and significant positive relationship ($r^2 = 0.52$, $p < 0.001$) observed between DMHg concentrations in the MBL and % ice cover, shown in Figure 3 - 4a, suggests that DMHg accumulated under sea ice may rapidly evade to the
atmosphere once the ice begins to break up. This observation reinforces the hypothesis that DMHg evasion from the ocean surface is the main source of DMHg in the MBL. In addition to diminishing sea-ice cover, enhanced production of DMHg in the surface mixed layer, with subsequent evasion to the atmosphere, is another possible explanation for the higher concentration of DMHg relative to MMHg in the CAA MBL. Indeed, the regions in the CAA, namely Lancaster Sound to Queen Maud Gulf, where highest DMHg concentrations were observed in both the MBL and water (Figure 3 - 3b, d), were also the regions in the Arctic with the highest PP due to the supply of nutrients from intense mixing [46]. Hg methylation occurring in oxic sea water has been linked to microorganism abundance and activity [6, 47] while higher DMHg production has previously been observed in highly productive zones [48]. This is supported by the strong positive relationship ($r^2 = 0.74, p < 0.01$) observed between PP rate and DMHg concentrations in the water column as shown in Figure 3 - 4b.

We posit that higher DMHg concentrations in the CAA MBL are due to higher marine DMHg production and its subsequent evasion to the atmosphere, which is enhanced from newly exposed ocean surface waters enriched with DMHg that accumulated during the ice-covered period.
Figure 3-4. Relationships between (a) dimethylmercury (DMHg) concentrations in the Arctic marine boundary layer (MBL) and % ice cover at time of sampling in HB and the Canadian Arctic Archipelago in 2010 (n = 17, 95% Slope Confidence Interval (CI) = 0.08 to 0.26), (b) DMHg concentrations in the MBL and primary production in the water column (n = 17, CI = 0.08 to 0.26) (c) MMHg concentrations in the MBL and % cloud cover (n = 36, CI = -0.098 to -0.019) and (d) DMHg concentration in the MBL and MMHg concentrations in surface seawater (n = 9, CI = -1.45 to -0.63). Lines plotted represent a linear regression. Level of significance: $p \leq 0.05$. 

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Sources of MMHg in the MBL

As discussed earlier, DMHg in the atmosphere is believed to be rapidly degraded to MMHg by photodemethylation reactions. While no significant relationship was found between MBL methylated Hg species and incident PAR (a proxy of total solar radiation), in our study, we observed a weak but significant negative relationship \( (r^2 = 0.20, p \leq 0.005) \) between MMHg concentrations in the MBL and extent of cloud cover (Figure 3 - 4c). These results suggest that MMHg production in the atmosphere is influenced by light in accordance with the hypothesis that light induced degradation of DMHg to MMHg is the main source of MMHg in the atmosphere. Furthermore, since the presence of cloud cover results in significant attenuation of short wave radiation due to light scattering [49], this observation suggests that in addition to radiation intensity, light spectral distribution might influence the extent of DMHg photodegradation to MMHg in the MBL.

Light driven reactions would be more important in HB, where radiation intensity and amplitude (Figure A2 - 6) is higher, than in the CAA because it is located at lower latitude. HB is also characterized by relatively higher DOC concentration in water (Table 3 - 1 and Figure A2 - 5). DOC affects bioavailability and stability of Hg by forming stable complexes, but may also influence methylation and thus production of MMHg and DMHg, in the water column by stimulating microbial activity. While volatilization of stable MMHg-DOC complexes from HB surface water is suspected to be insignificant, the enhanced DMHg production in water and its subsequent photodegradation in the atmosphere is a plausible mechanism for the predominance of MMHg in the HB MBL. The higher solar radiation intensity in HB is conducive to the photodegradation of DMHg in the atmosphere resulting in its depletion. In the CAA, on the other hand, the relatively lower
radiation intensity coupled with higher cloud cover might be less favorable to DMHg photodegradation resulting in less MMHg production.

While methylated Hg species in air showed significant relationships with ice cover and PP, no relation was observed between methylated Hg species and meteorological and oceanographic parameters known to influence seawater-air exchange, such as wind speed, air temperature or sea surface temperature and salinity (see Table A2 - 2). This lack of relation is however not surprising and is explained by the air sampling time resolution (3 hours), which was too low to capture a response to fast changing conditions (e.g., demethylation of DMHg and deposition of atmospheric MMHg). This also suggests that the presence of MMHg and DMHg in the atmosphere are not driven by the same factors, that these mechanisms are highly dynamic, or that air masses collected at low resolution integrate at a large scale, obscuring any site specific mechanisms.

*Atmospheric deposition of MMHg*

The identification and distribution of methylated Hg species in the Arctic MBL presented here represents an important contribution to our understanding of MMHg and DMHg cycling in the marine ecosystems. We hypothesize that the concentration of MMHg in air is not governed by a single mechanism, but rather several processes and reactions of varying importance. DMHg volatilization from open ocean surface is suggested to be an important mechanism controlling the cycling and sources of MMHg in marine environments. Atmospheric DMHg degradation remains a plausible mechanism for MMHg presence in the atmosphere. Surface water biogeochemical properties such as PP rates, DOC concentrations and ice cover are possibly important drivers for the presence of methylated Hg species in air as they all influence their flux across the seawater-air interface.
MMHg on sea spray, not measured in this study, is a potential additional source of MMHg in the atmosphere. Once in the air, MMHg may be released from the aerosol particle generating gaseous MMHg. Higher air sampling resolution, as well as controlled laboratory experiments, are required to better understand the factors controlling the presence and distribution of methylated Hg species in the Arctic MBL as well as the exchange and transformation mechanisms occurring at the seawater-air interface.

Regardless of production pathways, MMHg in the atmosphere represents a direct MMHg source to marine surface waters. This is supported by the significant negative relationship between DMHg concentrations in air and MMHg in surface water (Figure 3 - 4d) which suggests the atmospheric deposition of MMHg following its production from DMHg photodegradation.

Wet deposition is expected to be an important pathway for MMHg deposition since MMHg chloride complexes are quite soluble (water solubility: 5 g L\(^{-1}\)) [19] and would be readily scavenged from the atmosphere by precipitation. Assuming uniform vertical distribution of MMHg in the MBL above the Arctic Ocean, equilibrium between gaseous and aqueous phases of MMHg, and a gas-aqueous distribution coefficient of 0.9 \(\times\) 10\(^{-5}\) [40], the calculated concentrations of MMHg in precipitation for HB and CAA are 0.83 ± 0.52 ng L\(^{-1}\) and 0.4 ± 0.23 ng L\(^{-1}\), respectively (Table A2 - 3). These predicted concentrations are higher but consistent with those measured in Artic precipitation (< 0.008 – 0.18 ng L\(^{-1}\)) [50] and snow (0.02 – 0.281 ng L\(^{-1}\)) [17]. These values also agree with reports of MMHg in mid latitude precipitation (rain: 0.15 ng L\(^{-1}\) and snow: 0.05 ng L\(^{-1}\)) [51], boreal precipitation (0.07 – 0.31 ng L\(^{-1}\)) [52] as well as Californian Coast precipitation (rain: 0.1 ± 0.04 ng L\(^{-1}\) and fog: 3.4 ± 3.8 ng L\(^{-1}\)) [16]. Multiplying our estimated concentrations of MMHg in precipitation with the long term (~ 50 years) average summer (i.e. June to
August) precipitation volumes for HB and the CAA (225 mm and 93 mm respectively, Environment Canada Climate Data, [http://climate.weather.gc.ca/](http://climate.weather.gc.ca/) [53]), we estimate that average June to August MMHg wet deposition is 188 ± 117.5 ng m⁻² and 37 ± 21.7 ng m⁻² in these two regions (Table A2 - 3). These wet deposition rates of 1.5 ± 0.96 ng m⁻² d⁻¹ and 0.3 ± 0.18 ng m⁻² d⁻¹ for HB and the CAA represent a small portion of previously reported DMHg evasion flux estimates for HB and CAA (16.9 ng m⁻² d⁻¹ and 40 ng m⁻² d⁻¹, respectively) [10], suggesting that DMHg evasion from the ocean surface could easily sustain atmospheric MMHg concentrations and deposition.

Furthermore, we suspect that MMHg in the MBL would behave similarly to RGM, which has a fairly high dry deposition velocity (> 1 cm s⁻¹) [4]. MMHg is thus expected to be dry deposited either directly or adsorbed on aerosols relatively quickly (days to weeks). Dry deposition of MMHg has not been considered here but may be a potential additional atmospheric MMHg input to the ocean even though it is expected to be of lesser importance than wet deposition. As for DMHg, the calculated wet deposition from June to August is insignificant (4.5 pg m⁻² and 6.6 pg m⁻² for HB and CAA, respectively) which is not surprising considering its low water solubility and high volatility.

It should be noted that these values estimate potential fluxes during the summer season in the Arctic, when sea ice cover and darkness are minimal and precipitation constitutes > 40% of annual precipitation. It can therefore be safely argued that most of the annual atmospheric MMHg deposition will be occurring during this period. Due to drastic changes in light cycle and ice cover, different transformations mechanisms are expected during other seasons. DMHg accumulation in the atmosphere is expected over open water (e.g. polynyas and leads) in winter due to reduced photodegradation whereas higher atmospheric MMHg deposition in spring is a possibility. A previous study found a significant correlation
between concentrations of MMHg and Cl in Arctic spring snow, suggesting a marine source of MMHg from the evasion of DMHg from nearby polynyas and open ice leads [17]. The low MMHg deposition rates estimated above suggest that other processes such as *in situ* methylation might be more important in controlling MMHg concentrations in surface water. Nevertheless, estimations of depositional fluxes of MMHg are critically important in that MMHg deposition from the atmosphere to the open ocean contributes directly to the MMHg pool available for accumulation in the Arctic food web.

Furthermore, since gas exchange is probably one of the important mechanisms controlling the presence of methylated Hg species in the atmosphere and the deposition of MMHg to the ocean, the important physical changes occurring in the Arctic including the decrease of ice cover of 3.2% per decade ([https://nsidc.org/arcticseaicenews/](https://nsidc.org/arcticseaicenews/)) [54] and shorter sea ice season might change the magnitude of this exchange mechanism and, thus, affect the bioaccumulation of MMHg in the Arctic marine ecosystem.

**Supplementary Information**

Supplementary information associated with this article can be found, in Appendix 2.
Literature Cited


CHAPTER 4: METHYLATION AND DEMETHYLATION OF MERCURY IN POLAR MARINE WATERS
Abstract

Monomethylmercury (MMHg) concentrations in water controls the bio-accumulation rate and fate of mercury (Hg) in the Arctic marine ecosystem. MMHg is a potent neurotoxin and poses serious health risk to the local populations who traditionally feed on marine mammals and fish. The sources of MMHg in Arctic waters are still unclear and in situ methylation has been proposed as a potential mechanism controlling MMHg concentrations. Incubation experiments using isotopically labelled Hg species, namely inorganic Hg (Hg(II)), MMHg and dimethylmercury (DMHg), were conducted in the Canadian Arctic Archipelago and Hudson Bay surface waters to assess methylation and demethylation potentials. Methylation of Hg(II) to MMHg as well as DMHg demethylation to MMHg were observed in the absence of light and the presence of oxygen. We report experimentally derived rate constants for MMHg methylation ($0.92 \pm 0.82 \times 10^{-3} \text{ d}^{-1}$) and demethylation ($0.35 \pm 0.25 \text{ d}^{-1}$). For the first time, we determined a demethylation rate constant for DMHg ($0.98 \pm 0.51 \text{ d}^{-1}$) and demonstrated MMHg production from DMHg demethylation at a rate of $0.04 \pm 0.02 \text{ d}^{-1}$. These results suggest that DMHg can be a source of MMHg in Arctic surface waters and that MMHg and DMHg concentrations in Arctic and sub-Arctic surface waters are influenced by different factors or methylation pathways. DMHg production was strongly linked to biological activity and primary productivity while MMHg methylation seemed to be influenced by numerous factors including DMHg demethylation rate and water physico-chemical properties.

Keywords— Arctic Ocean, methylmercury, methylation, demethylation, stable isotopes.
Introduction

Arctic marine organisms have elevated concentrations of mercury (Hg) posing a health threat to the local population who traditionally feed on marine derived food [174]. Hg is most readily assimilated by marine organisms and bio-accumulated through food webs in the form of monomethylmercury (MMHg), a potent neurotoxin. In the Arctic marine ecosystem, MMHg constitutes > 85% of total Hg in fish and top predators [52, 224]. Atmospheric wet and dry deposition is the dominant source of inorganic Hg (II) to marine environments [159, 160, 204]. Deposited Hg(II), if not photoreduced to Hg⁰ [71, 125], is methylated, mainly to monomethylmercury (MMHg) and dimethylmercury (DMHg). The concentration of methylated Hg species in water is governed by methylation and demethylation reactions, two key processes controlling the fate of Hg in the Arctic marine ecosystem.

Methylation of Hg(II) occurs by both biotic [179] and abiotic [14] mechanisms in primarily anoxic environments. Biotic methylation is mediated primarily by sulfate-reducing bacteria [97, 105] and occurs mainly under anoxic conditions such as the water sediment interface [12]. Abiotic methylation is believed to occur in the presence of methyl donors such as methylcobalamin [14]. In marine ecosystems, biotic methylation of Hg(II) is likely the main pathway since methylated Hg in subsurface water has been linked to particulate organic matter remineralization which most probably provides substrate for methylation and drives microbial activity. Furthermore, maximum methyl Hg concentrations suggest that methylation mainly occurs in the oxygen minimum zone [159, 164, 205, 225]. Demethylation processes of DMHg and MMHg in the marine environment are believed to follow different pathways and the end products remain unclear. Degradation of DMHg is
supposedly mainly abiotic and photochemically-driven, while MMHg decomposition is mainly microbially mediated. Abiotic photochemical demethylation of MMHg occurs by the cleavage of the carbon-Hg bond by UV radiation as well as visible light [123-125]. Biotic MMHg demethylation occurs either by the oxidative pathways, where methanogens and sulfate reducers convert the methyl group of MMHg to Hg (II) and carbon dioxide [121] or reductive processes where demethylation and reduction of MMHg to methane and Hg(0) is catalyzed by enzymes, namely organomercury lyase and reductase, related to the mer operon in bacteria [93, 120].

While the numerous studies on the distribution of methylated Hg species in ocean waters ([204] and references therein) have improved our understanding of the biogeochemical cycling of mercury (Hg) and the methylation potential in the water column, the sources of MMHg and DMHg in surface water is still unclear. Potential sources include vertical transport of methylated Hg species from deeper production zones by upwelling [159], direct input of externally formed methylated Hg from the atmosphere [145] or rivers [153, 226] and in situ methylation of Hg(II) [160, 227]. Recent experiments, using the novel technique of Hg stable isotopes as tracers [36], have reported Hg methylation, in Arctic [104] and Mediterranean [103] surface waters, but not in coastal Atlantic waters [95]. However, the importance of DMHg as an indirect source of MMHg is still unclear. Indeed, it has been suggested that DMHg is the primary biogenic methylation product in polar marine waters [138] and that its decomposition is a potential source of MMHg [159-161]. This hypothesis has not been tested experimentally mainly due to the challenges of handling highly toxic DMHg.

Using isotope enriched Hg, we conducted incubation experiments in Arctic and sub-Arctic marine waters to examine (i) the methylation potential in surface water and (ii) the
importance of DMHg degradation as a source of MMHg. Isotope enriched additions of reactive Hg ($^{200}$Hg(II)), monomethylmercury ($^{199}$Hg) and dimethylmercury ($^{198}$Hg) were used at sub-ambient concentrations to examine simultaneous methylation (i.e., formation of $^{200}$MMHg, $^{200}$DMHg and $^{199}$DMHg) and demethylation (i.e., loss of $^{199}$MMHg and of $^{198}$DMHg) processes in water. The transformations of the stable isotope spikes as well as the behaviour of ambient methylated Hg species are discussed and methylation and demethylation rate constants for MMHg and DMHg are calculated. Finally, we suggest that biological activity and water properties are important parameters affecting the presence and stability of methylated Hg species in Arctic surface waters.
Methods

Study site description

Water sampling

Seawater samples were collected at six stations in Hudson Bay (HB) and five stations in the Canadian Arctic Archipelago (CAA), in summer 2010 and 2011 respectively, on board the CCGS research icebreaker *Amundsen*. Sea water samples were collected with a carousel water sampler (Sea-Bird 32) equipped with 12 L Teflon® lined Niskin-type bottles (OceanTest Equipment), according to recommended protocols for trace metals [184, 207] at the subsurface chlorophyll maximum (SCM). The SCM depth was chosen as elevated Hg concentrations have been recorded in these biologically important zones, in polar marine waters [138]. Seawater for incubation assays was slowly decanted in pre-cleaned 1.2 L glass bottles by allowing twice the volume of the container to flow slowly into the bottles to preserve the water redox conditions at sampling. The bottle was capped immediately and stored at 4°C in the dark for incubation experiments, which were performed within 2 h after sampling. Seawater was also collected in acid cleaned glass bottles at the surface (2 m) and at the bottom of the water column (~ 10 m above sediment surface) for MMHg determination. Details of the sampling location and depths are given in supplementary Table A3 - 1.

Spiking and incubation

To assess the production and loss of methylated Hg species in sea water, known concentrations of isotope enriched MM\(^{199}\)Hg (as CH\(_3^{199}\)HgCl at 0.4 ng L\(^{-1}\) in 2010 only), \(^{200}\)Hg (II) (as \(^{200}\)Hg(NO\(_3\))\(_2\) at 40 ng L\(^{-1}\) in 2010 and 20 ng L\(^{-1}\) in 2011), and DM\(^{198}\)Hg
(0.015 ng L\(^{-1}\) in 2010 and 0.030 ng L\(^{-1}\) in 2011) were added to water samples. \(^{200}\)Hg was added to monitor methylation to MMHg and DMHg, MMHg loss and methylation to DMHg was assessed by measuring decrease in added MM\(^{199}\)Hg concentration and any DM\(^{199}\)Hg formed. Finally, DM\(^{198}\)Hg was added to assess DMHg demethylation and to determine specific rate constants. Spiking solutions of \(^{200}\)Hg(II) and MM\(^{199}\)Hg were freshly prepared for each incubation experiment by diluting known volumes of the stock solutions using sea water and injected through an aperture in the sample bottle using a high precision microsyringe (Hamilton). The spiking solutions for each assay were kept in bromine chloride solution for concentrations determination (as total Hg) in the laboratory to obtain the exact concentrations added. The assays were performed in triplicates and samples were incubated in the dark at 4°C for intervals of 0, 12 and 24 h.

At the end of the incubation time, the samples were purged with Hg-free argon gas (12 L) to displace DMHg, which was trapped on carbotraps situated at the outlet of the purging vessel. A sodalime trap was used in front of the carbotrap to reduce moisture interferences that may lower the traps collection efficiency. The carbotraps were flushed with Hg-free Argon before storage to remove any moisture present. The carbotraps were tightly capped, double bagged and stored in acid cleaned glass containers at -20°C in the dark until analysis. After purging, a subsample (375 ml) was transferred from each bottle into pre-cleaned 500 ml glass bottle which was tightly capped with Teflon lined caps, double bagged and stored at -20°C for MMHg determination. While freezing of water sample reduces risks of artifactual formation of MMHg during storage, as previously reported in the case for acidification [149, 188], freezing of the water samples is not immediate. In our case, complete freezing was observed a few hours after storage in the freezer (~ 6 hours). Due to the slow and gradual freezing of the samples, reactions and transformations might have
continued during the freezing period (~5 h). The sea water samples were analysed for
MMHg using isotope dilution after distillation and aqueous phase ethylation, separation by
gas chromatography (GC) and detection by inductively coupled mass spectrometry (ICP-
MS) [36]. DMHg on carbotraps were determined by thermodesorption and analysed by
GC-ICP-MS [206]. The analytical methods are detailed in the Supplementary Information.
The absolute detection limit expressed as 3 times the standard deviation of the standard
blanks was 0.5 pg l⁻¹. The precision of the isotope ratios measurement ranged between
0.5 – 1.2 % relative standard deviation (RSD) and was calculated from daily MMHg
standards. The absolute detection limit for individual isotopes (¹⁹⁸Hg, ¹⁹⁹Hg, ²⁰⁰Hg) is
0.04 pg or better (calculated from MMHg standards of 10 pg). The limits of detection of
MMHg transformations were 0.2, 0.3 and 0.1 pg l⁻¹ for MM¹⁹⁹Hg, MM²⁰⁰Hg and MM¹⁹⁸Hg,
respectively.

**Methylation and demethylation rate determination**

A schematic of the transformation pathways investigated and the enriched Hg isotopes used
for the incubation experiment is depicted in Figure 4 - 1b. Demethylation rates (k_d) were
determined from the loss of methylated Hg species. MM¹⁹⁹Hg loss was monitored for
MMHg demethylation and demethylation rate constants of MM¹⁹⁹Hg (k_d₁) were calculated
according to equation 1 adapted from Hintelmann et al. (2000) [156]:

\[
[MM^{199}Hg] = [MM^{199}Hg]_0 e^{-k_d t}
\]  

(1)

Where [MM¹⁹⁹Hg] is the concentration of newly generated MM¹⁹⁹Hg (pg L⁻¹), [MM¹⁹⁹Hg]₀
is the concentration of MM¹⁹⁹Hg (pg L⁻¹) added at the start of incubation, k_d is specific
demethylation rate constant (per day, d⁻¹), and t is incubation time (in days).
DMHg demethylation rate constant \((k_{d2})\) was determined from the loss of \(\text{DM}^{198}\text{Hg}\) according to equation 2.

\[
[\text{DM}^{198}\text{Hg}] = [\text{DM}^{198}\text{Hg}]_0 e^{-k_{d2}t} \tag{2}
\]

DMHg demethylation to MMHg \((k_{d3})\) was assessed by monitoring the production of \(\text{MM}^{198}\text{Hg}\) from \(\text{DM}^{198}\text{Hg}\).

The specific methylation rate constants \((k_m)\) for MMHg \((k_{m1})\) and DMHg \((k_{m2})\) formation were determined by assessing \(\text{MM}^{200}\text{Hg}\) and \(\text{DM}^{200}\text{Hg}\) production from \(\text{Hg(II)}^{200}\) the spike while \(\text{DM}^{199}\text{Hg}\) methylation rate constant \((k_{m3})\) was derived from the \(\text{MM}^{199}\text{Hg}\) spike experiment.

The net \(\text{MM}^{200}\text{Hg}\) production rate which is the sum of \(\text{MM}^{200}\text{Hg}\) production from \(\text{Hg(II)}^{200}\) methylation and \(\text{MM}^{200}\text{Hg}\) loss by demethylation is expressed by the following equation:

\[
\frac{d[\text{MM}^{200}\text{Hg}]}{dt} = k_m[\text{Hg(II)}^{200}] - k_d[\text{MM}^{200}\text{Hg}] 
\]

Assuming that the \(\text{Hg(II)}\) concentration remained essentially constant during the 24 h incubation period, the rate constant for \(\text{MM}^{200}\text{Hg}\) methylation \((k_{m1})\) was thus obtained by solving the following differential equation:

\[
\frac{d[\text{MM}^{200}\text{Hg}]}{dt} = k_{m1}[\text{Hg(II)}^{200}] \tag{3}
\]

Equation 2 was also applied for calculating the overall \(\text{DM}^{200}\text{Hg}\) methylation rate \((k_{m2})\) constant from \(\text{Hg(II)}^{200}\) and for the \(\text{DM}^{199}\text{Hg}\) methylation rate constant \((k_{m3})\) obtained from the \(\text{MM}^{199}\text{Hg}\) addition experiment.
**Ancillary Data and calculations**

Vertical profiles of oceanographic variables were obtained with a CTD rosette equipped with sensors to measure temperature and salinity (Sea-Bird 911plus), dissolved oxygen (Sea-Bird SBE43) and in vivo fluorescence (SeaPoint Chlorophyll Fluorometer). Water samples were collected for dissolved organic carbon (DOC), known to influence Hg availability and methylation, at the SCM depth. The DOC sample processing and analysis protocol are detailed in the Supplementary Information. Chlorophyll $a$ concentrations and net primary production (PP) rates were also measured using the fluorometric method (Turner Designs 10-AU fluorometer) and the 14C-uptake method, respectively. The procedures are detailed elsewhere [208]. The surface mixed layer depth was determined as the depth with maximum value of the Brunt - Väisälä frequency ($N^2$) which was calculated from the density gradient [209]. Nutrient concentrations namely nitrate ($\text{NO}_3^-$), nitrite ($\text{NO}_2^-$), phosphate ($\text{PO}_4^{3-}$), and silicic acid ($\text{Si(OH)}_4$) were measured immediately after sampling using a Bran-Luebbe 3 autoanalyzer (adapted from Grasshoff et al. 2009) [228].
Figure 4-1. (a) Seawater sampling locations for mercury methylation and demethylation experiments performed on board the research icebreaker *CCGS Amundsen* in July 2010 in Hudson Bay and July 2011 in Canadian Arctic Archipelago. (b) Schematic showing the isotope enriched mercury species used for the determination of methylation ($k_m$) and demethylation ($k_d$) rate constants of monomethylmercury (MMHg) and dimethylmercury (DMHg).
Results and discussion

Biogeochemical characteristics and ambient methylated Hg species concentrations

The main oceanographic parameters characterising Hudson Bay (HB) and the Canadian Arctic Archipelago (CAA), the two regions where incubation experiments were conducted in 2010 and 2011 respectively, are presented in Table 4 - 1. The depth of the subsurface chlorophyll maximum (SCM), where water was sampled, was similar in both regions, averaging 30 ± 14 m and 26 ± 5 m in HB and CAA respectively. However, the SCM depth varied greatly in HB (range: 15 m – 50 m) while in CAA, the SCM depth was more constant (range: 20 m – 32 m). Chlorophyll a (chl a) concentrations at the SCM were also lower in HB (2.6 ± 2.9 μg l⁻¹) compared to CAA (7.7 ± 9.4 μg l⁻¹, Table 4 - 1). The base of the euphotic zone (arbitrarily chosen as the depth with 1 % surface irradiance) was slightly below the SCM, averaging 36±11 m and 37±10 m in HB and CAA respectively. Higher light attenuation was observed for SCM depths at HB sampling locations (1 to 5 % of photosynthetically active radiation, PAR) than in CAA (50 – 10 % PAR). Light is attenuated by chromophoric dissolved organic matter (CDOM) [220] which is the light absorbing fraction of dissolved organic carbon (DOC). DOC concentrations were higher in HB compared to CAA due to river inputs. The influence of freshwater inputs from Nelson River (stations 705 and 705a) and James Bay (station 702) in HB is also translated by lower salinity (< 30 PSU) and higher water temperature (> 1°C) (Table 4 - 1). The depth profiles of temperature, salinity, density, oxygen and chl a from surface water to 10 m above the bottom depth at the different stations are shown in the supplementary information (Figure A3 - 1). Nutrient concentrations (namely nitrate, silicate and ammonium) were lower at the sampling locations in HB compared to CAA (Table A3 - 1).
MMHg concentrations in HB waters (at the SCM depth) were significantly higher (t-test, p < 0.05) than DMHg concentrations averaging 20.0 ± 12.5 pg L⁻¹ and 5.6 ± 4.1 pg L⁻¹, respectively. No significant difference was observed between methylated Hg species in CAA waters with average concentrations of 21.2 ± 13.75 pg L⁻¹ and 13.9 ± 8.9 pg L⁻¹ for MMHg and DMHg respectively. Furthermore, MMHg was present in higher proportion than DMHg in almost all the samples as shown in Figure 4 - 2. Concentrations of MMHg and DMHg are given in Table A3 - 2.
Table 4-1. Oceanographic parameters at sampling stations where incubations experiments were performed in Hudson Bay (HB) in 2010 and the Canadian Arctic Archipelago (CAA) in 2011.

<table>
<thead>
<tr>
<th>Station</th>
<th>Sampling Depth (m)</th>
<th>T (° C)</th>
<th>Salinity (PSU)</th>
<th>Mixed layer depth (m)</th>
<th>Euphotic zone (m)</th>
<th>% Irradiance at SCM</th>
<th>O₂ (ml L⁻¹)</th>
<th>Chla (µg L⁻¹)</th>
<th>PP (mg C m⁻³ d⁻¹)</th>
<th>DOC (µmol L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>702</td>
<td>27</td>
<td>1.2</td>
<td>28</td>
<td>17</td>
<td>26</td>
<td>1</td>
<td>8.1</td>
<td>0.9</td>
<td>10.5</td>
<td>120.3</td>
</tr>
<tr>
<td>707</td>
<td>50</td>
<td>-1.5</td>
<td>32</td>
<td>16</td>
<td>49</td>
<td>1</td>
<td>7.3</td>
<td>7.7</td>
<td>6.3</td>
<td>115.5</td>
</tr>
<tr>
<td>706</td>
<td>40</td>
<td>-1.5</td>
<td>32</td>
<td>11</td>
<td>44</td>
<td>1</td>
<td>7.3</td>
<td>7.3</td>
<td>1.1</td>
<td>92.6</td>
</tr>
<tr>
<td>705a</td>
<td>15</td>
<td>1.2</td>
<td>29</td>
<td>2</td>
<td>24</td>
<td>5</td>
<td>7.8</td>
<td>0.9</td>
<td>5.6</td>
<td>120.0</td>
</tr>
<tr>
<td>705</td>
<td>14</td>
<td>2.0</td>
<td>29</td>
<td>10</td>
<td>34</td>
<td>5</td>
<td>7.9</td>
<td>0.6</td>
<td>3.4</td>
<td>na</td>
</tr>
<tr>
<td>850</td>
<td>32</td>
<td>-0.8</td>
<td>31</td>
<td>14</td>
<td>27</td>
<td>na*</td>
<td>7.8</td>
<td>4.6</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td>HB</td>
<td>30 ± 14</td>
<td>0.1 ± 1.5</td>
<td>30 ± 2</td>
<td>12 ± 5</td>
<td>36 ± 11</td>
<td>3 ± 2</td>
<td>7.7 ± 0.3</td>
<td>2.6 ± 2.9</td>
<td>5.2 ± 3.8</td>
<td>112.1 ± 13.2</td>
</tr>
<tr>
<td>175</td>
<td>20</td>
<td>-1.1</td>
<td>32</td>
<td>11</td>
<td>38</td>
<td>na*</td>
<td>8.3</td>
<td>1.5</td>
<td>NA</td>
<td>68.5</td>
</tr>
<tr>
<td>160</td>
<td>25</td>
<td>-0.7</td>
<td>32</td>
<td>3</td>
<td>50</td>
<td>50</td>
<td>8.0</td>
<td>0.4</td>
<td>7.9</td>
<td>68.1</td>
</tr>
<tr>
<td>331</td>
<td>26</td>
<td>-0.7</td>
<td>32</td>
<td>6</td>
<td>27</td>
<td>na*</td>
<td>8.3</td>
<td>8.1</td>
<td>na</td>
<td>75.5</td>
</tr>
<tr>
<td>310</td>
<td>32</td>
<td>-1.2</td>
<td>31</td>
<td>3</td>
<td>34</td>
<td>10</td>
<td>8.1</td>
<td>20.9</td>
<td>66.3</td>
<td>71.7</td>
</tr>
<tr>
<td>CAA</td>
<td>26 ± 5</td>
<td>0.9 ± 0.3</td>
<td>32 ± 0</td>
<td>6 ± 4</td>
<td>37 ± 10</td>
<td>30 ± 28</td>
<td>8.2 ± 0.2</td>
<td>7.7 ± 9.4</td>
<td>37.1 ± 41.3</td>
<td>70.9 ± 3.4</td>
</tr>
</tbody>
</table>

*not available.

Table 4-2. Ambient monomethylmercury (MMHg) and dimethylmercury (DMHg) concentrations and rate constants of MMHg and DMHg demethylation ($k_d$) and methylation ($k_m$) in sub-arctic (Hudson Bay, HB) and Arctic (Canadian Arctic Archipelago, CAA) marine waters.

<table>
<thead>
<tr>
<th>Station</th>
<th>MMHg (pg L$^{-1}$)</th>
<th>DMHg (pg L$^{-1}$)</th>
<th>$k_{d1}$,amb. (d$^{-1}$)</th>
<th>$k_d1$ (d$^{-1}$)</th>
<th>$k_d2$,amb. (d$^{-1}$)</th>
<th>$k_d2$ (d$^{-1}$)</th>
<th>$k_d3$ (d$^{-1}$)</th>
<th>$k_m1$ (x 10$^{-3}$ d$^{-1}$)</th>
<th>$k_m3$ (x 10$^{-3}$ d$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>702</td>
<td>22.0 ± 10.24</td>
<td>3.6 ± 1.02</td>
<td>nd‡</td>
<td>nd</td>
<td>1.29</td>
<td>1.27</td>
<td>nd</td>
<td>3.02</td>
<td>7.83</td>
</tr>
<tr>
<td>707</td>
<td>28.6 ± 6.14</td>
<td>13.8 ± 3.00</td>
<td>nd</td>
<td>0.14</td>
<td>2.54</td>
<td>1.38</td>
<td>nd</td>
<td>0.84</td>
<td>2.98</td>
</tr>
<tr>
<td>706</td>
<td>14.6 ± 2.29</td>
<td>4.18 ± 1.60</td>
<td>0.92§</td>
<td>0.14</td>
<td>0.33</td>
<td>nd</td>
<td>nd</td>
<td>0.97</td>
<td>1.24</td>
</tr>
<tr>
<td>705a</td>
<td>5.0 ± 2.94</td>
<td>4.4 ± 0.35</td>
<td>0.6§</td>
<td>0.53</td>
<td>na</td>
<td>na</td>
<td>nd</td>
<td>0.59</td>
<td>na</td>
</tr>
<tr>
<td>705</td>
<td>39.1</td>
<td>2.53 ± 0.30</td>
<td>1.96§</td>
<td>nd</td>
<td>na</td>
<td>na</td>
<td>nd</td>
<td>1.09</td>
<td>na</td>
</tr>
<tr>
<td>850</td>
<td>11.2 ± 0.58</td>
<td>5.1 ± 0.74</td>
<td>nd</td>
<td>0.60</td>
<td>na</td>
<td>na</td>
<td>nd</td>
<td>1.22</td>
<td>na</td>
</tr>
<tr>
<td>HB</td>
<td>20.0 ± 12.5</td>
<td>5.6 ± 4.1</td>
<td>1.16 ± 0.71*0.35 ± 0.25</td>
<td>1.39 ± 1.11</td>
<td>1.32 ± 0.08</td>
<td>nd</td>
<td>1.3 ± 0.87</td>
<td>4.0 ± 3.4</td>
<td></td>
</tr>
<tr>
<td>175</td>
<td>41.3 ± 14.90</td>
<td>5.2 ± 1.12</td>
<td>1.97</td>
<td>na‡</td>
<td>nd</td>
<td>1.54</td>
<td>0.06</td>
<td>0.27</td>
<td>na</td>
</tr>
<tr>
<td>160</td>
<td>12.5 ± 2.49</td>
<td>9.4 ± 0.16</td>
<td>0.87</td>
<td>na</td>
<td>0.09</td>
<td>0.64</td>
<td>0.04</td>
<td>0.49</td>
<td>na</td>
</tr>
<tr>
<td>331</td>
<td>18.7 ± 4.23</td>
<td>15.1 ± 3.97</td>
<td>1.63</td>
<td>na</td>
<td>nd</td>
<td>0.36</td>
<td>0.03</td>
<td>0.58</td>
<td>na</td>
</tr>
<tr>
<td>310</td>
<td>12.2 ± 8.19</td>
<td>25.8 ± 4.04</td>
<td>0.82</td>
<td>na</td>
<td>0.27</td>
<td>0.33</td>
<td>0.02</td>
<td>0.13</td>
<td>na</td>
</tr>
<tr>
<td>CAA</td>
<td>21.2 ± 13.75</td>
<td>13.9 ± 8.9</td>
<td>1.32 ± 0.57</td>
<td>na</td>
<td>0.18 ± 0.13</td>
<td>0.72 ± 0.57</td>
<td>0.04 ± 0.02</td>
<td>0.37 ± 0.20</td>
<td>na</td>
</tr>
<tr>
<td>Overall</td>
<td>20.5 ± 12.3</td>
<td>9.0 ± 7.0</td>
<td>1.25 ± 0.58</td>
<td>0.35 ± 0.25</td>
<td>0.9 ± 1.0</td>
<td>0.98 ± 0.51</td>
<td>0.04 ± 0.02</td>
<td>0.92 ± 0.82</td>
<td>4.0 ± 3.4</td>
</tr>
</tbody>
</table>
*Mean ± sd. † not detected. ‡ not available. $k$: rate constants. $^\$k_d$ values determined over 0-12 h interval.

$k_{d1}$amb.: Ambient MMHg demethylation, $k_{d1}$: MM$^{199}$Hg demethylation, $k_{d2}$amb.: Ambient DMHg demethylation, $k_{d2}$: DM$^{198}$Hg demethylation, $k_{d3}$: DM$^{198}$Hg demethylation to MM$^{198}$Hg, $k_{m1}$: MM$^{200}$Hg methylation from $^{200}$Hg(II) and $k_{m3}$: DM$^{199}$Hg methylation from MM$^{199}$Hg(II).

Note: $k_{m2}$ DM$^{200}$Hg methylation from $^{200}$Hg(II) is not included since concentrations of DM$^{200}$Hg were too close to MDL.
Figure 4-2. Monomethylmercury (MMHg) and dimethylmercury (DMHg) concentrations at stations (at the subsurface chlorophyll maximum ~ 30 m) where methylation and demethylation experiments were conducted.
**MMHg demethylation**

During the incubation assays, the concentrations of ambient MMHg decreased rapidly over the 0 – 12 h interval for HB samples (Figure 4 - 3a) and then seemed to stabilize or even increase during the 12 – 24 h interval. The loss in MMHg with time was more constant in CAA samples (Figure 4 - 3b) during 24 h incubation interval. Increase in MMHg concentrations observed during the 12 – 24 h interval could possibly be due to MMHg release from biogenic particles or decaying organic matter.

The ambient MMHg demethylation rate constant \((k_{dlamb.})\) averaged 1.16 ± 0.71 d\(^{-1}\) in HB and 1.32 ± 0.57 d\(^{-1}\) in CAA (Table 4 - 2). It is noteworthy that demethylation rate constants calculated from ambient MMHg concentrations represent the net methylation rate i.e., the balance between MMHg loss and MMHg production. Ambient MMHg demethylation rate constants were significantly and positively correlated with concentrations \((r^2 = 0.882, p < 0.005, \text{Figure A3 - 2})\) suggesting that MMHg loss is favored at high concentrations. It is suspected that MMHg is degraded to Hg(II) rather than methylated to DMHg since no correlation was observed between the MMHg loss and DMHg concentrations. This is supported by previous studies which demonstrated that demethylation of methylmercury to Hg(II), followed by reduction to Hg\(^0\), is biologically mediated involving reductive [93, 120] or oxidative pathways [121].

Note: For 2010, ambient MMHg demethylation rate \((k_{dlamb})\) was calculated over the 0–12 h interval instead of the 24 h interval due to suspected MMHg production during the 12–24 h interval.

Demethylation was also observed for MM\(^{199}\)Hg spiked in water samples which was performed in HB water only (Figure 4 - 3c). The demethylation rate constants \((k_{dl})\) obtained from spiked MM\(^{199}\)Hg, averaged 0.35 ± 0.25 d\(^{-1}\). These demethylation rate constants are similar to those reported in the only previous study investigating MMHg demethylation in...
arctic marine waters (0.28 ± 0.05 d⁻¹ at the SCM depth) [104]. Demethylation of MMHg in the absence of light was also reported in a study in Atlantic water but was of lesser extent than photochemical reduction [95]. A study investigating MMHg demethylation rates in the Mediterranean Sea (at the SCM depth) also reported comparable values (0.03 – 0.11 d⁻¹) without light while demethylation rates under a diurnal radiation regime were roughly two fold higher (0.06 – 0.25 d⁻¹) [103] demonstrating that demethylation was both photochemically and microbially mediated. A photodemethylation rate constant in Arctic surface waters has been estimated to be 0.04 d⁻¹ [104]. These results suggest that photodemethylation is not the primary pathway driving MMHg demethylation in Arctic surface waters, especially at the base of the euphotic zone, and that demethylation is mainly biologically or chemically mediated.

The demethylation rate constant for MMHg, determined from the loss of spiked MM^{199}Hg (as CH$_3^{199}$HgCl), is lower than ambient MMHg net demethylation rate which is the product of simultaneous MMHg loss and production. In natural waters, ambient MMHg is comprised of a mixture of CH$_3$Hg$^+$ complexes (e.g. CH$_3$HgCl, CH$_3$HgBr, CH$_3$HgOH), with varying stability and thus demethylation rate constants, while only CH$_3^{199}$HgCl was spiked for the incubation assay. The net demethylation rate constants reported here is thus relevant for CH$_3$HgCl only and would reflect demethylation rates in waters where CH$_3$HgCl is the dominant MMHg species. The higher demethylation rate for ambient MMHg could thus be explained by the faster demethylation rate of other MMHg complexes present in natural water, e.g., CH$_3$HgOH, compared to CH$_3$HgCl.

The reduction of MM$^{199}$Hg and $^{200}$Hg(II) was also assessed by measuring dissolved elemental Hg (Hg$^0$) concentration in water, but unfortunately, due to $^{200}$Hg$^0$ contamination,
the data were not always reliable. However, general observations indicate that a large portion of Hg\textsuperscript{200} was rapidly reduced to Hg\textsuperscript{0}.

Figure 4-3. Ambient monomethylmercury (MMHg) concentrations with time in (a) Hudson Bay and (b) the Canadian Arctic Archipelago surface waters (subsurface chlorophyll maximum) and (c) isotope enriched MMHg (MM\textsuperscript{199}Hg) with time in HB surface water during incubation experiments. MM\textsuperscript{199}Hg shown as the percentage of MM\textsuperscript{199}Hg initially added (~400 pg L\textsuperscript{-1}).
Ambient DMHg loss was observed for most samples (Figure 4 - 4a-b) with average DMHg net demethylation rate constants (\(k_{d2\text{amb.}}\)) of 1.39 ± 1.11 d\(^{-1}\) and 0.18 ± 0.13 d\(^{-1}\) for HB and CAA waters, respectively (Table 4 - 3). As for the spiked DMHg (DM\(^{198}\)Hg), the decrease in concentrations with time was less constant since for some stations, a slight increase was observed during the 12 – 24 h incubation interval (Figure 4 - 4c-d). Nevertheless, when considering 0 – 12 h incubation interval, the DM\(^{198}\)Hg gross demethylation rate (\(k_{d2}\)) averaged 1.32 ± 0.08 d\(^{-1}\) and 0.72 ± 0.57 d\(^{-1}\) for HB and CAA, respectively (Table 4 - 2). The DMHg demethylation rate constants presented here are higher than previous estimates of DMHg degradation ranging from 1.9 x 10\(^{-4}\) d\(^{-1}\) [166] to 0.32 d\(^{-1}\) [159].

In HB, the net demethylation rate constant is similar to the gross demethylation rate suggesting that demethylation is the main process controlling DMHg concentrations in HB waters. In CAA however, the lower net demethylation rate suggests that simultaneous DMHg production is partially compensating for DMHg demethylation. The lower net demethylation in CAA compared to HB is reflected by the higher ambient concentrations in CAA (Table 4 - 2 and Figure 4 - 2).

These results, obtained from incubations under dark conditions, demonstrate that similarly to MMHg, DMHg demethylation in Arctic waters is not exclusively photochemically driven and that DMHg degradation is also microbi ally or chemically mediated. This is of significant importance since the general consensus in the literature suggests that DMHg concentration in water is controlled primarily by photodemethylaton. Furthermore, since in Arctic waters SCMs are located at depths with low light availability (1 – 5% and 10 – 50% of surface irradiance in HB and CAA respectively), photodemethylation is expected to be of lesser importance while biotic demethylation would be most significant. This would also
suggest that in the Arctic Ocean, demethylation also occurs under ice cover or during the polar night of winter months when sunlight is absent.

We also observed the formation of MM$^{198}\text{Hg}$ from DM$^{198}\text{Hg}$ (1.9 – 6.3% of the available DM$^{198}\text{Hg}$) after 24 h incubation in CAA samples (Figure 4 - 5) but not in HB samples. We suspect that any potentially formed MM$^{198}\text{Hg}$ in HB was below the method detection limit and thus not detected. The average demethylation rate constant of DMHg to MMHg averaged 0.04 ± 0.02 d$^{-1}$ in CAA waters. These results demonstrate for the first time that DMHg degradation can be a source of MMHg in water confirming previous hypotheses that MMHg is the product of DMHg degradation [159, 161].
Figure 4-4. Ambient dimethylmercury (DMHg) stability with time for water samples in (a) Hudson Bay in 2010 and (b) the Canadian Arctic Archipelago (CAA) in 2011. % Isotope enriched DMHg (DM$^{198}$Hg) from the water samples at regular incubation intervals in (c) HB and (d) CAA.
Figure 4-5. % Monomethylmercury (MM$^{198}$Hg) production from DM$^{198}$Hg spike over 24 hours in the Canadian Arctic Archipelago waters (at the subsurface chlorophyll maximum depth).
Methylation of Hg(II) and MMHg methylation rate constants \((k_m)\)

Methylation of \(^{200}\text{Hg}\)(II) resulting in the production of \(^{200}\text{MMHg}\) was observed for all the incubations assays (Figure 4 - 6) in accordance with the limited number of studies investigating methylation in surface water [12, 26]. A significant positive relationship \((r^2 = 0.68, p < 0.01, \text{Figure A4 - 3a})\) was found between newly formed \(^{200}\text{MMHg}\) (from \(^{200}\text{Hg}\)(II) spike) and ambient \(\text{MMHg}\) concentrations suggesting that \(\text{MMHg}\) production from added spike is a reliable indicator of the standing pool of \(\text{MMHg}\) in a given water body. Interestingly, highest \(^{200}\text{MMHg}\) production \((0.04 \pm 0.02\% \ ^{200}\text{Hg}\)(II)) was observed at “zero” hours. While these samples were put in the freezer immediately after adding the spike, it took up to 5 hours, until samples were completely frozen and all methylation reactions stopped completely. This is consistent with a previous study, which reported instantaneous \(\text{MMHg}\) production from \(\text{Hg(II)}\), but at much higher rates \((0.03–0.25\%)\) [104] than those reported here \((0.01 – 0.06\%)\). Instantaneous methylation of \(^{200}\text{Hg}\)(II) to \(^{200}\text{MMHg}\) was higher in HB samples \((0.05 \pm 0.02\% \ ^{200}\text{Hg}\)(II)) compared to CAA \((0.02 \pm 0.01\% \ ^{200}\text{Hg}\)(II)) while ambient \(\text{MMHg}\) concentrations in these two regions were not significantly different. Since higher amount of \(^{200}\text{Hg}\)(II) were amended in HB samples, these observations suggest that \(\text{Hg(II)}\) concentration might be an important driver controlling the rate of methylation to \(\text{MMHg}\) as previously hypothesized [160]. HB water is also characterized by higher DOC content which may promote the abiotic formation of \(\text{MMHg}\) by providing methyl groups [14] for methylation, although it may also affect \(\text{Hg(II)}\) substrate availability due to complexation with reduced sulfur of organic matter [118]. The positive influence of DOC on methylation is translated by the significant relationship between the fraction of \(^{200}\text{MMHg}\) and DOC \((r^2 = 0.549, p < 0.05, \text{Figure S3b})\) as well as...
MM$^{200}\text{Hg}$ methylation rate ($r^2 = 0.79$, $p < 0.1$). These results strongly suggest that DOC concentrations might be influencing MM$^{200}\text{Hg}$ production in HB.

However, we observed a decrease in net production of MM$^{200}\text{Hg}$ with time and for some stations as early as 12 h after start of incubation (Figure 4 - 6). Reduced production rate during the 12 – 24 h interval was also observed in a previous study and attributed to increasing MMHg demethylation rate as MMHg concentration increased [104]. This is consistent with our earlier observation where the ambient MMHg demethylation rate was positively correlated with MMHg concentrations. The net loss of MM$^{200}\text{Hg}$ with time observed in our study might thus be the combined result of reduced $^{200}\text{Hg(II)}$ availability as well as increasing simultaneous demethylation of newly produced MM$^{200}\text{Hg}$ as incubation progressed.

Average rate constants of MM$^{200}\text{Hg}$ production ($k_{m1}$) at the SCM in HB and CAA were $0.0013 \pm 0.0009 \text{ d}^{-1}$ and $0.00037 \pm 0.0002 \text{ d}^{-1}$ respectively (Table 4 - 3). These values are lower than the previous methylation rate reported for Arctic marine waters ($0.006 \pm 0.002 \text{ d}^{-1}$) [104]. However, these methylation rate constants are not directly comparable since changes in Hg(II) concentrations were taken into account in the previous study while we assumed constant Hg(II) concentrations. Nonetheless, our results demonstrate the direct production of MMHg from both Hg(II) methylation and DMHg demethylation.
Figure 4-6. Production of monomethylmercury (MM\textsuperscript{200}Hg) from \textsuperscript{200}Hg(II) spike in seawater at the subsurface chlorophyll maximum depths (~ 30m) in (a) Hudson Bay in 2010 (40 ng \textsuperscript{200}Hg\textsuperscript{2+}) and (b) the Canadian Arctic Archipelago in 2011 (20 ng \textsuperscript{200}Hg\textsuperscript{2+}) over 24 hours (0, 12, 24 hours intervals).

**DM\textsubscript{Hg} production and methylation rate constants**

Methylation of \textsuperscript{200}Hg(II) to DM\textsuperscript{200}Hg was very slow and even though DM\textsuperscript{200}Hg was detected after 24 hours incubation, DM\textsuperscript{200}Hg concentrations were very close or below the MDL indicating insignificant DM\textsuperscript{200}Hg production from \textsuperscript{200}Hg(II) during the incubation period. The net DM\textsubscript{Hg} production from Hg(II) is thus much lower than MM\textsubscript{Hg} production since MM\textsuperscript{200}Hg production was observed only a few hours after \textsuperscript{200}Hg(II) spiking in both HB and CAA as mentioned earlier. This is supported by the higher proportion of ambient MM\textsubscript{Hg} compared to DM\textsubscript{Hg} at almost all sampling stations (Figure 4 - 2) both in HB (MM\textsubscript{Hg} : DM\textsubscript{Hg} = 5) and CAA (MM\textsubscript{Hg}:DM\textsubscript{Hg} = 6). These observations do not agree with previous studies, which suggested that DM\textsubscript{Hg} is the primary product of Hg(II) methylation [138, 159]. However, DM\textsuperscript{200}Hg production from \textsuperscript{200}Hg (0.0003 d\textsuperscript{-1}, data not shown) was observed at the most productive station (Stn. 310, Figure A3 - 1) suggesting
that DMHg production might be at least of minor importance in highly productive zones. Indeed, it has been suggested that DMHg production is closely tied to primary productivity [138]. Previous studies have reported much higher DMHg production rates from Hg(II) under similar conditions in surface waters in the Arctic Ocean (0.006 d\(^{-1}\)) [104] and Mediterranean sea (0.005-0.015 d\(^{-1}\)) [103].

Furthermore, DM\(^{199}\)Hg production from MM\(^{199}\)Hg, at a rate of 0.004 ± 0.003 d\(^{-1}\) was also observed during the assays in HB (Figure 4 - 7) suggesting that MMHg methylation is another source of DMHg in surface water. DMHg production from MMHg was also observed in a previous study but at much lower rate (maximum 0.0016 d\(^{-1}\) at the SCM) [104] than reported here. The higher rate constants for Hg(II) methylation to MMHg (\(k_{m1}\)) and MMHg methylation to DMHg (\(k_{m3}\)) than direct Hg(II) methylation to DMHg (\(k_{m2}\)) suggest that DMHg production occurs mainly in two steps involving firstly MMHg production from Hg(II) and secondly DMHg production from MMHg rather than through the one-step mechanism of DMHg production from Hg(II).
Figure 4-7. Production of dimethylmercury (DM$^{199}$Hg) from MM$^{199}$Hg spike in Hudson Bay waters at subsurface chlorophyll maximum depths (~ 30m) over 24 hours (0, 12, 24 hours intervals).

**Factors affecting methylated Hg species methylation and demethylation**

Methylated Hg production has been linked to biological activity based on the relationship between methylated Hg species and apparent oxygen utilization and/or phosphate, both proxies of heterotrophic organic matter remineralisation [159, 164, 205]. We tested the relationship among methylated Hg methylation and demethylation rate constants and environmental variables by performing a correlation analysis (Spearman’s ρ); those with significant correlations are presented in Table A3 - 4. The significant parameters were used to perform a principal component analysis (PCA) and the analysis revealed that two principal components (PC1 and PC2) explained 83.1% of the total variation (Figure 4 - 8).
Figure 4-8. PCA analysis of parameters explaining variations in monomethylmercury (MMHg) methylation rate \( (k_{m1}) \) and dimethylmercury (DMHg) demethylation rate \( (k_{d2}) \). Chl \( a \): Chlorophyll \( a \), DOC: dissolved organic content and T: sea water temperature at subsurface chlorophyll maximum depth.

The first component (PC1; 50.8%) was related to primary productivity variables namely Chl \( a \), DOC and temperature (Table A3 - 5). DMHg concentrations, which explained most of the variation in PC1, was associated with Chl \( a \), which is an indicator for bioactivity in the water column. As expected from the PCA, DMHg was significantly correlated with both Chl \( a \) \( (r^2 = 0.96, p < 0.001) \) and primary productivity \( (r^2 = 0.79, p < 0.01) \). A closer look at the phytoplankton composition showed that DMHg had a stronger relationship with large phytoplankton \( (\geq 5 \mu m) \) biomass and production rather than with small phytoplankton \( (0.7 – 5 \mu m) \) as shown in Figure A3 - 4a-b.
These results suggest that DMHg concentration is almost exclusively driven by biological (autotrophic) activity and productivity, with higher DMHg production associated with large phytoplankton. This hypothesis is consistent with our earlier observation of DMHg production in highly productive water as well as previous studies which reported methylated Hg in regions of high productivity [170] and linked DMHg production to biological [138] and more specifically polar macro algal activity [167]. A possible mechanism for phytoplankton associated aerobic methylation by transmethylation reactions involved in the degradation of phytoplankton osmolyte dimethylsulfoniopropionate (DMSP) has been proposed in a recent study [229].

The second most important parameter for PC1, methylation rate constant ($k_{m1}$), was associated with DOC concentrations and temperature (Figure 4 - 8). DOC sustains heterotrophic activity while temperature is known to influence microbial activity in general. MMHg methylation rate constant ($k_{m1}$) was significantly correlated to water temperature ($r^2 = 0.91$, $p < 0.05$) and DOC concentrations ($r^2 = 0.79$, $p < 0.1$). The positive influence of temperature on MMHg methylation rate constant, also suggested in a previous study [103], is most probably due to enhanced biological activity with increasing temperature while DOC influences methylation either directly by providing substrate for Hg methylation and/or methyl donors or indirectly by enhancing microbial activity.

The second component (PC2; 32.3%) was related to OM remineralization with phosphate as the main environmental factor and MMHg concentrations as well as DMHg demethylation rate constant ($k_{d2}$) as the main parameters explaining the variation (Table A4 - 5). Overall, MMHg showed a weak correlation with phosphorus ($r^2 = 0.57$) but showed a strong significant correlation with DMHg demethylation rate constant, $k_{d2}$ ($r^2 = 0.85$, $p < 0.05$, Figure A3 - 5). These results support the hypothesis that MMHg production is
linked to OM remineralisation, which sustains heterogeneous microbial activity, but also suggest that while MMHg production from heterogeneous activity is possible, DMHg demethylation might be an important pathway for MMHg production in Arctic waters. Furthermore, while overall no significant relationship was found between DMHg and phosphorus, a significant correlation was observed between DMHg and phosphorus ($r^2 = 0.94$, $p < 0.05$) in HB. The positive relationship between DMHg and phosphorus in HB suggests that processes such as OM remineralization can influence DMHg production in oligotrophic waters, where bacterial biomass is greater relative to phytoplankton [230]. However, the relationship between DMHg and Chl $a$ discussed earlier suggests that under eutrophic conditions, i.e., when nutrients supply is not the limiting factor for microbial activity, autotrophic activity might be of greater importance in controlling DMHg concentrations.

This study demonstrates that in Arctic and sub-Arctic marine waters, Hg(II) is methylated to produce both MMHg and DMHg and that degradation of methylated Hg species is not exclusively photo driven. MMHg production in Arctic Ocean surface waters seems to be governed by heterotrophic (mainly bacterial) methylation as well as DMHg demethylation production. The sources of DMHg are, however, less clear; DMHg production seems to be closely linked to autotrophic microbial activity and primary productivity and is favored under eutrophic conditions, where large size phytoplankton is predominant. Finally, the high demethylation rate and relatively low methylation rates of DMHg suggest that other factors such as microbial composition or mechanisms other than in situ methylation influence DMHg production in surface waters.
Supporting Information

Supporting Information available: Detailed procedures and additional figures and tables.
Literature Cited


CHAPTER 5: CONCLUSIONS

Monomethylmercury (MMHg) is the most toxic form of mercury (Hg) as it biocaccumulates in biota and is efficiently transferred along food webs. MMHg is mainly produced in aquatic environments, by biotic and abiotic processes, and the consumption of marine food such as fish is the main route of exposure to humans [53]. Hg concentrations in Arctic fish and marine mammals are amongst the highest in the world [52, 173] and are often above the safe consumption guidelines (0.5 μg g⁻¹) posing a health threat to the local populations who consume these organisms as part of their traditional diet [174, 175]. The increasing concerns about the bioaccumulation and biomagnification of MMHg in Arctic marine mammals demand a better understanding of the sources and biogeochemical cycling of MMHg in the Arctic marine environment. The source of MMHg to the Arctic Ocean remains uncertain and proposed potential sources include atmospheric deposition [145] and in situ production in the water column [104, 160, 227]. The main focus of my research presented in this thesis was to investigate the importance of these proposed sources and the factors controlling these processes so as to improve our understanding of sources and sinks of MMHg in the Arctic marine environment. The main findings are discussed below.

A method for the measurement of methylated Hg species in the atmosphere

Even though methylated Hg species are present in the atmosphere, there are very few reports on concentration measurements due to the analytical challenges associated with the sampling and quantification of ultra-trace levels of MMHg and DMHg in air. The work presented in chapter 2 tackles this problem by investigating the suitability of commercially available adsorbents for the measurement of gaseous MMHg and DMHg by solid phase adsorption. A new generation of divinylbenzene (DVB), Bond Elut ENV (BE), is evaluated
for the first time for solid phase adsorption of methylated Hg species and its performance is compared against two commonly used adsorbents namely Carbotrap®B (CB) and Tenax®TA (TA). BE proved to be suitable both for collection and analysis offering high sampling capacity as well as very good chromatographic properties. I thus propose BE as an alternative to both TA and CB, two adsorbents commonly used in the laboratory for collecting of volatile methylated Hg species from aqueous solutions, especially for situations where extended sample purging or delayed analysis of collected species is mandated. Using BE as an adsorbent in collection traps, as much as 150 L of air at a flow rate of 1.5 L min⁻¹ could be sampled at 4°C and stored for up to two months at -20°C without significant loss of MMHg or DMHg.

While this study shows that BE has the desired adsorbent characteristics for the simultaneous sampling of MMHg and DMHg in air, future work should focus on lowering the sampling resolution and the method detection limit. The reliable measurement of trace concentrations still requires the sampling of relatively large volumes of air. The resulting sampling times of a few hours are too long to capture short term transformations and sampling of particular, well constrained air masses. Higher sampling resolution could be achieved by employing higher sampling flow rates with larger diameter tubes or different mesh size of adsorbent. Lower temperature and even cryogenic trapping with liquid nitrogen [231, 232] could be tested to further improve the trapping efficiency. Better separation of Hg species peaks, especially Hg(0) and DMHg, could be achieved by employing cryogenic gas chromatography [190, 233], capillary gas chromatography [234-237] or multicapillary gas chromatography [232, 238]. Finally, more precise results may be achieved with the use of species specific isotope dilution [186, 239] for calibration. Simultaneous sampling of well defined isotope enriched spike additions could be used to
monitor and correct for losses and transformations that might occur during the different sampling steps, particularly during online ethylation, adsorbent trapping and storage.

**Methylated Hg species in the atmosphere and their main drivers**

The method developed and described above was successfully adapted and used for the measurement of methylated Hg species in air above the Arctic Ocean as presented in chapter 3. For the first time, I present the measurement of concentrations of methylated Hg species in the Arctic marine boundary layer which range from < 0.5 (LOQ) to 12.7 pg m\(^{-3}\) for MMHg and < 0.5 to 11.3 pg m\(^{-3}\) for DMHg. The potential factors controlling the presence and spatial distribution of methylated Hg species in air were also investigated. My data support the hypothesis that the main mechanism responsible for the presence of DMHg in air seems to be evasion from ocean water, where DMHg is produced. The data also suggest that the main factors influencing DMHg concentrations in air are sea ice cover and primary productivity. DMHg seems to be a precursor of MMHg and the photochemically driven demethylation of DMHg in the atmosphere is proposed to be the main source of MMHg in the atmosphere. Estimations of MMHg wet deposition suggest that the atmosphere contributes to a small fraction of MMHg in surface water. However, deposition of MMHg bound to aerosols, which was not taken into account during the measurements might be an additional source of MMHg to surface water.

While this study for the first time conclusively demonstrates the presence of methylated Hg in the Arctic atmosphere in summer, it also raises some questions regarding the behaviour of methylated Hg species over longer time periods. The Arctic environment is characterized by strong seasonality with quasi total darkness, extensive sea ice cover, very cold temperature and a rather stable boundary layer during winter. In summer, there is 24 h
daylight and partial loss or thinning of sea ice. Since DMHg destruction and MMHg formation in the atmosphere seem to be influenced by photolytic reactions, a completely different scenario on the extent and distribution of methylated Hg species can be expected during winter months. The stable atmosphere, lack of photo reactions and suspected continuous gas exchange in open water polynyas in winter might result in the accumulation of DMHg in the Arctic atmosphere while lower MMHg concentration or even its depletion in the atmosphere is a possibility during winter. The onset of spring in the arctic atmosphere is characterised by AMDEs, a phenomenon which involves enhanced oxidation of GEM to RGM due to polar sunrise and the presence of oxidants in the atmosphere [68, 133]. A similar behaviour for DMHg i.e. the photodemethylation of DMHg to MMHg is a possibility and should be investigated. The production of MMHg and its deposition might not be at its maximum in the middle of summer, when sampling for this study was conducted, but rather at the polar sunrise. These questions and hypotheses could be addressed by (i) performing long term measurements, particularly at the beginning and end of major seasonal events e.g polar sunrise, ice break up, maximum darkness in winter and also (ii) lower sampling resolution that would allow the monitoring of methylated Hg concentrations in response to changing environmental conditions.

This study suggests that the exchange of DMHg between the ocean surface and the atmosphere is an important process for the atmospheric cycling and environmental turnover of methylated Hg species in the Arctic marine ecosystem. However, there is a paucity of data on DMHg fluxes from the ocean surface and reported values are mainly from calculation estimations [150, 167] justifying uncertainties regarding its atmospheric contribution. Future activities on the fate of methylated Hg species in the Arctic marine environment should therefore concentrate on the processes at the ocean-air interface,
particularly better estimations of DMHg flux from the ocean to assess its importance. Direct flux measurements of DMHg from the ocean surface are essential a better understanding of the behaviour of DMHg and the environmental parameters controlling its evasion. DMHg flux measurement could be achieved by adapting existing approaches for the measurement of other gaseous Hg species fluxes from water surfaces which include dynamic flux chamber methods [240-242] and micrometeorological methods such as the relaxed eddy accumulation (REA) [243].

This study also highlights the importance of sea ice cover as a factor controlling the DMHg flux to the atmosphere. However, a better understanding of the role of sea ice in the exchange of DMHg to the atmosphere is still required; whether sea ice influences DMHg evasion (i) by acting solely as a physical barrier to gas exchange and light penetration or (ii) by being itself an additional source of DMHg to the atmosphere due to the production of DMHg within the ice pack still needs to be clarified. Furthermore, the behaviour of DMHg in the MBL during the transition from a complete sea-ice cover to its gradual receding needs to be further investigated. Finally the influence of other environmental parameters on the evasion of DMHg from the ocean, such as wind speed, waves amplitude, sea and air temperature, need to be determined to better predict the behaviour of DMHg at the ocean-atmosphere interface with changing seasons and climate.

Methylated Hg sources and sinks in Arctic Ocean surface water

The other proposed source of methylated Hg species in ocean surface water, i.e in situ methylation of Hg(II), was investigated by performing incubation experiments using isotope enriched mercury species, described in Chapter 4. The fate of MMHg and DMHg
were also investigated with the aim to obtain a more complete understanding of the methylation and demethylation pathways. While instantaneous methylation of Hg(II) to both MMHg and DMHg, was observed, MMHg was produced at a much faster rate (0.00092 ± 0.0002 d⁻¹) than DMHg. I propose that Hg(II) methylation is the main mechanism controlling concentrations of MMHg while DMHg production might occur in two-steps, involving the formation of MMHg as an intermediate product. It is also possible that the conditions prevailing during the incubation experiment were not conducive to DMHg production. However, formation of MMHg from DMHg was also demonstrated suggesting that the steady state concentrations of methylated Hg species in surface water is the net product of simultaneous formation and loss. From my results I propose that MMHg concentrations are thus the net result of (i) formation by methylation of Hg(II) and demethylation of DMHg, and (ii) loss by demethylation to Hg(II) and methylation to DMHg. Furthermore, the instantaneous production of MMHg and DMHg and limited production observed over longer periods (12 and 24 h) suggests that initial methylation of Hg(II) is very rapid and that future similar experiments should be conducted with higher resolution (shorter incubation times) to better capture the transformations.

Photochemical demethylation might be an important degradation process that controls concentrations of methylated Hg species in the Arctic Ocean surface water. Photo-induced demethylation has mainly been studied in Arctic lakes and ponds e.g. [123, 143, 244] and less so in ocean water. More work is necessary to better determine the kinetics photo-demethylation process(es) in ocean water. In addition, a characterization of the kinetics of photo-demethylation in relation to water properties (e.g. dissolved organic matter content) in various aquatic environment would improve significantly model predictions regarding its importance. Photo-induced demethylation is particularly relevant to the Arctic Ocean
since quasi continuous sunlight prevails during summer. Furthermore, the importance of photo-demethylation processes might increase in the near future, with increasing sea-ice loss resulting in new and longer ocean surface exposition to solar radiation.

DMHg concentrations were closely linked to primary productivity and phytoplanktonic biomass, in both air (Chapter 3) and water (Chapter 4), reinforcing the hypothesis of its biogenic origin. Previous studies have indeed suggested the production of DMHg from phytoplankton and bacteria in marine polar surface waters [138] while more recently, the involvement of phytoplankton osmolyte dimethylsulfiniopropionate (DMSP) in aerobic Hg methylation has been proposed [229]. These findings challenge the paradigm that methylated Hg species are produced only by bacteria, under anaerobic conditions, and accentuate the need for further studies on the mechanistic aspects of Hg methylation in the Arctic. Future studies should also investigate the role of phytoplankton and photosynthetic bacteria e.g. cyanobacteria, in the methylation of Hg(II) in oxic waters. Furthermore, in light of the significant relationship between atmospheric DMHg and ice-cover (chapter 3), the possible production of DMHg by sea ice algae is another mechanism worth investigating. Biological activity, which is linked to methylated Hg production in this research, has a strong seasonal signature in the Arctic Ocean, with maximum production at the start of summer, decrease in production due to nutrient depletion and the return of sea ice in fall, and finally virtually insignificant production during winter due to the presence of sea ice and the absence of light [245]. This raises the question of seasonal methylation and demethylation transformations in the water column and whether a pattern similar to biological productivity can be expected for MMHg net production. Future studies can address these questions by performing sampling campaigns during the different seasons in the Arctic Ocean and under sea ice, if logistics permits, or by conducting mesocosm and
laboratory studies. The research presented in this thesis offers some insights to the potential mechanisms governing the presence of methylated Hg species in the Arctic marine environment, both in the boundary layer and in surface water of the Arctic Ocean. To confirm or infirm the hypotheses put forth and improve our understanding of the biogeochemical cycle of methylated Hg, future studies should aim at investigating (i) the kinetics of Hg species methylation and demethylation over lower time resolution, especially the demethylation of DMHg to MMHg, with the use of novel techniques such as isotope enriched spikes, (ii) the sites and conditions favoring DMHg production in the water column and finally (iii) the implication of phytoplankton and ice fauna, e.g. ice algae and bacteria, in DMHg production.

**Mercury and climate change in Arctic**

The vulnerability of the Arctic ecosystem to Hg contamination is intricately linked to the drastic and rapid climate change that this part of the globe is facing. Arctic air temperature has been increasing in an unprecedented fashion over the past decades (+1 – 3°C from 2000 to 2005) [246] impacting severely other Arctic environmental compartments. Sea ice loss in the Arctic is occurring much faster than forecasted with record minimum sea ice extent reported twice over the last decade (in 2007 and 2012) [223]. Sea ice extent is now decreasing at a rate of 9 – 10% per decade [247, 248] implying that the Arctic Ocean, which is mostly covered by first year ice, will probably be largely ice-free in late summer in a few decades. The other consequences of the warming of the Arctic include melting of glaciers and ice caps, thawing of permafrost as well as increase in precipitation [50].

Climate change (and its associated impacts on the environment) is already having discernable effects on transport pathways, speciation and cycling of Hg within the Arctic
ecosystem and may further increase Arctic ecosystem and human exposure to mercury. Among the numerous alarming consequences, an exacerbation of the vulnerability of the Arctic ecosystem to Hg contamination is predicted (see [176, 177] for reviews). Even though it is difficult to predict the effect of climate change on Hg contamination in the Arctic, several scenarios can be modelled. The increase in air temperature will likely result in increased Hg oxidation in the atmosphere [50] while increasing precipitation will enhance scavenging from the atmosphere and deposition, thus increasing the input of Hg (including MMHg) to the increasing ice free ocean. Increase in coastal erosion [249, 250] and river discharge [251, 252], due to the combined effect of glaciers melting, permafrost thawing and increased precipitation might also increase the input of riverine and terrestrial Hg to coastal regions of the Arctic Ocean. Greater input of Hg to the Arctic Ocean increases the pool of Hg available for methylation and MMHg production. However, the standing pool of Hg in the Arctic Ocean Hg might be depleted by enhanced photoreduction and photodemethylation caused by increasing irradiation reaching surface water due to the disappearance or thinning of sea ice. Hg(0) produced from photoreaction will rapidly evade to the atmosphere by gas exchange which is also expected to increase with increasing water and air temperature. The warmer and ice free growing season in the Arctic Ocean might also promote primary productivity [253] thus impacting biotic Hg transformations e.g. reduction/oxidation and methylation/demethylation cycles, resulting possibly in a net increase in MMHg production.

The possible scenarios mentioned above clearly demonstrate that the net influence of climate change on MMHg production is complex and the transformations interwoven, stressing the importance of better understanding the mechanisms and factors affecting MMHg formation and fate. A better, more complete understanding of the cycle of MMHg
is critical to predict the extent of Hg contamination in the Arctic and develop appropriate management strategies to minimize the risk of Hg exposure to the local population which relies on marine food for their subsistence living.
Literature Cited


APPENDIX 1: SUPPORTING INFORMATION FOR “EVALUATION AND OPTIMIZATION OF SOLID ADSORBENTS FOR THE SAMPLING OF GASEOUS METHYLATED MERCURY SPECIES”

Table A1 - 1. Specifications of adsorbent traps (Tenax® TA, Bond Elut ENV, Carbotrap® B and Carbosieve® S-III) evaluated for gaseous organic mercury sampling.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Tenax® TA</th>
<th>Bond Elut ENV</th>
<th>Carbotrap® B</th>
<th>Carbosieve S-III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>2,6-diphenyl-p-phenylene oxide</td>
<td>styrene-divinylbenzene</td>
<td>Graphitized Carbon Black</td>
<td>Carbon Molecular Sieve</td>
</tr>
<tr>
<td>Amount (g)</td>
<td>0.1</td>
<td>0.075</td>
<td>0.4</td>
<td>0.5</td>
</tr>
<tr>
<td>Mesh size (µm)</td>
<td>20/35</td>
<td>125</td>
<td>20/40</td>
<td>60/80</td>
</tr>
<tr>
<td>Inner Diameter (ID) of tube (mm)</td>
<td>4</td>
<td>5</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Length of Bed (mm)</td>
<td>42</td>
<td>20</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Surface area (m² g⁻¹)</td>
<td>35</td>
<td>500</td>
<td>~100</td>
<td>~975</td>
</tr>
<tr>
<td>Desorption temperature (°C)</td>
<td>245</td>
<td>245</td>
<td>245</td>
<td>245</td>
</tr>
<tr>
<td>Max Temperature (°C)</td>
<td>350</td>
<td>245</td>
<td>&gt; 400</td>
<td>&gt; 400</td>
</tr>
</tbody>
</table>

a specifications as provided by manufacturer
Figure A1 - 1. Schematic set up for breakthrough volume determination of collection traps.
Figure A1 - 2. Schematic for sampling of monomethylmercury (MMHg) and dimethylmercury (DMHg) in air by online ethylation (for MMHg only) and preconcentration on solid adsorbent traps.
Table A1 - 2. Precision and detection limits for sampling of monomethylmercury on Tenax® TA and Bond Elut ENV traps and quantification by solid phase adsorption thermodesorption (TD) – gas chromatography (GC) - inductively coupled plasma mass spectrometry (ICP/MS).

<table>
<thead>
<tr>
<th>Expected amount (pg)</th>
<th>Tenax® TA</th>
<th>Bond Elut ENV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Amount Mean ± SD (pg)</td>
<td>% RSD</td>
</tr>
<tr>
<td>250</td>
<td>250 ± 6.5</td>
<td>3%</td>
</tr>
<tr>
<td>30</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>10.5 ± 1.1</td>
<td>10%</td>
</tr>
<tr>
<td>5</td>
<td>5.3 ± 0.4</td>
<td>7%</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>1.4 ± 0.2</td>
<td>14%</td>
</tr>
<tr>
<td>0.5</td>
<td>0.7 ± 0.04</td>
<td>5%</td>
</tr>
</tbody>
</table>

| Blank                | 0.1 ± 0.05 |
| Limit of detection (LOD)\(^a\) | 0.15 pg |
| Limit of Quantitation (LOQ)\(^b\) | 0.5 pg |

SD - one standard deviation, RSD - Relative Standard deviation

\(^a\) LOD = 3 x SD (Blank)

\(^b\) LOQ = 10 x SD (Blank)
Table A1 - 3. Monomethylmercury (MMHg) and dimethylmercury (DMHg) recoveries (%, mean) from Tenax® TA (TA), Bond Elut ENV (BE), Carbotrap® B (CB), Carbosieve® SIII (CS) and mixed adsorbents (CB/BE and CB/T) traps.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>MMHg % Recovery</th>
<th>SD</th>
<th>% RSD</th>
<th>n</th>
<th>DMHg % Recovery</th>
<th>SD</th>
<th>% RSD</th>
<th>n</th>
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<tr>
<td>TA</td>
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<td>9.2</td>
<td>9</td>
<td>25</td>
<td>95</td>
<td>8.1</td>
<td>9</td>
<td>11</td>
</tr>
<tr>
<td>CB</td>
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<td>72</td>
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<td>0.3</td>
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<td>18</td>
<td>3</td>
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<tr>
<td>CB/BE</td>
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<td>1</td>
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<tr>
<td>CB/TA</td>
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<td>3</td>
<td>99</td>
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<td>1</td>
<td>3</td>
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SD - one standard deviation, RSD - relative standard deviation
Table A1 - 4. Effect of temperature (4°C and 21°C) and increasing volume on organic mercury recovery (%) from adsorbent traps (monomethylmercury for Tenax® TA and Bond Elut ENV and dimethylmercury for Carbotrap® B).

<table>
<thead>
<tr>
<th>Volume (L)</th>
<th>Tenax® TA (4 °C)</th>
<th>Tenax® TA (21 °C)</th>
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<tbody>
<tr>
<td></td>
<td>% Recovery</td>
<td>SD</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>-</td>
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<tr>
<td>4</td>
<td>100</td>
<td>0.2</td>
</tr>
<tr>
<td>5</td>
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<tr>
<td>6</td>
<td>-</td>
<td>-</td>
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<td>8</td>
<td>98</td>
<td>0.4</td>
</tr>
<tr>
<td>10</td>
<td>97</td>
<td>2.4</td>
</tr>
<tr>
<td>12</td>
<td>98</td>
<td>1.3</td>
</tr>
<tr>
<td>15</td>
<td>98</td>
<td>0.8</td>
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<td>99</td>
<td>0.1</td>
</tr>
<tr>
<td>30</td>
<td>92</td>
<td>7.1</td>
</tr>
<tr>
<td>40</td>
<td>91</td>
<td>2.8</td>
</tr>
<tr>
<td>65</td>
<td>85</td>
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</tr>
<tr>
<td>80</td>
<td>78</td>
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<tr>
<td>100</td>
<td>69</td>
<td>5.0</td>
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<table>
<thead>
<tr>
<th>Volume (L)</th>
<th>Bond Elut ENV (4 °C)</th>
<th>Bond Elut ENV (21 °C)</th>
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<tr>
<td></td>
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<td>SD</td>
</tr>
<tr>
<td>30</td>
<td>-</td>
<td>-</td>
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<td>-</td>
<td>-</td>
</tr>
<tr>
<td>55</td>
<td>102</td>
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<td>65</td>
<td>101</td>
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<tr>
<td>75</td>
<td>-</td>
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</tr>
<tr>
<td>80</td>
<td>101</td>
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<tr>
<td>100</td>
<td>100</td>
<td>4.4</td>
</tr>
<tr>
<td>200</td>
<td>91</td>
<td>6.1</td>
</tr>
<tr>
<td>&gt; 300</td>
<td>97</td>
<td>11.9</td>
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Table A1 - 4 (continued)

<table>
<thead>
<tr>
<th>Volume (L)</th>
<th>% Recovery</th>
<th>SD</th>
<th>% RSD</th>
<th>p value</th>
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<td>100</td>
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<tr>
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</table>

Carbotrap® B (4 °C)

Recovery - mean, SD - one standard deviation, % RSD - Relative standard deviation, n ≥ 3

Means were statistically different at p ≤ 0.05
Table A1 - 5. Monomethylmercury recovery (% mean) from Tenax® TA collection and backup traps with increasing volume at 4°C and 21°C.

<table>
<thead>
<tr>
<th>Volume (L)</th>
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<th>3rd Backup trap</th>
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<tr>
<td></td>
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<td>SD</td>
<td>% Recovery</td>
<td>SD</td>
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<tr>
<td>4L</td>
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<td>0</td>
<td>0.2</td>
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<tr>
<td>8L</td>
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<td>0.4</td>
<td>1</td>
<td>0.4</td>
</tr>
<tr>
<td>12L</td>
<td>98</td>
<td>1.3</td>
<td>2</td>
<td>1.3</td>
</tr>
<tr>
<td>15L</td>
<td>98</td>
<td>0.8</td>
<td>2</td>
<td>0.8</td>
</tr>
<tr>
<td>20L</td>
<td>99</td>
<td>0.1</td>
<td>1</td>
<td>0.1</td>
</tr>
<tr>
<td>28L</td>
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<td>0.0</td>
<td>2</td>
<td>0.0</td>
</tr>
<tr>
<td>40L</td>
<td>91</td>
<td>3.8</td>
<td>7</td>
<td>4.8</td>
</tr>
<tr>
<td>100L</td>
<td>69</td>
<td>5.0</td>
<td>19</td>
<td>16.1</td>
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<tr>
<td>120L</td>
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<td>18</td>
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<table>
<thead>
<tr>
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<tbody>
<tr>
<td>3L</td>
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<td>5L</td>
<td>98</td>
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<tr>
<td>6L</td>
<td>92</td>
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<tr>
<td>15L</td>
<td>83</td>
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</table>

SD - one standard deviation
APPENDIX 2: SUPPORTING INFORMATION FOR “DETERMINATION OF MONOMETHYLMERCURY AND DIMETHYLMERCURY IN THE ARCTIC MARINE BOUNDARY LAYER”

Study Area

Hudson Bay (HB) is an inland sea that is connected to the Atlantic Ocean via the Hudson Strait and the Labrador Sea, and to the Arctic Ocean via the Foxe Basin in the Canadian Arctic Archipelago (CAA). HB is relatively shallow (mean depth of 103 m [1], roughly ranging between 30 – 300 m), has a semi-annual ice cover and is greatly influenced by large river discharge volume (~700 km³ yr⁻¹) [2]. River discharge, namely from the Nelson and Churchill rivers in the southwest, and Moose, Albany and La Grande rivers in James Bay, contributes very high load of terrestrial organic matter and nutrients to the system. Freshwater from rivers and melting ice constitutes the HB Summer Surface Water (HBSSW), the upper layer of the water column, below which lies the HB Intermediate Water (HBIW) and the Hudson Strait Bottom Water (HBSBW). The HBSBW is a homogeneous mixture of Baffin Bay and Intermediate Labrador Sea Water. The CAA, on the other hand, is characterized by narrow channels and deeper basins due to the relatively narrow continental shelf, thus resulting in mixing of Pacific waters entering from the west (e.g. McClure Strait) and Atlantic waters from Baffin Bay through Lancaster Sound [3]. In contrast to HB, there are no major rivers in the CAA and freshwater input is mainly from melting ice, which contributes to the polar mixed layer (PML) at the surface. Water masses in the CAA also include a colder, fresher and nutrient richer layer of Pacific waters above more saline and warmer Atlantic waters [4]. Most of the CAA (Barrow Strait, Peel Sound,
Queen Maud Gulf) is covered by landfast sea ice during the ice season except for at the mouth of Lancaster Sound where there is open water [5, 6].

Methods

Methylated mercury species sampling by online ethylation and solid phase adsorption

The air pump and the ethylation system were located in a heated container and connected to the sampling inlet located at the bow of the ship by the sampling line, which was insulated using polyethylene foam tubes usually used for pipe insulation in households. Two manifolds were used at the sampling inlet to increase the spatial integration in the sampling plane[7, 8].

To reduce potential interferences associated with the relatively long run of the sampling line, the air pump was kept running as much as possible and started at least 2 hours before sampling to allow air circulation in the sampling line. The sampling line consisted entirely of Teflon® tubing (Cole Parmer) and fittings to minimize Hg sorption to surfaces. A Teflon® filter (47 mm diameter; 0.45 µm) was used at the sample line inlet to remove particulate matter that might deposit along the sampling line. A particulate filter (0.45 µm) is commonly used at sample inlets for gaseous mercury measurement[9]. The filter at the sampling inlet was changed every four days to minimize the risk of Hg loss by adsorption on particles or sea aerosols that might be present on the filter. Furthermore, prior to the sampling campaign and every 2 weeks during sampling, the sampling line and inlet were acid-washed according to recommended methods[10] to reduce any risk of contamination due to particle (<0.45 µm) deposition. Similar measures were employed in previous studies, which reported reliable Hg species concentrations in air when sampling lines of similar length were used (up to 10 m) e.g., [11-14]
Monomethylmercury (MMHg) species were derivatized to volatile ethylmethylmercury prior to collection on solid adsorbent traps by passing the air stream through an ethylation filter. The ethylation filter was prepared immediately before use by allowing 50 µL of sodium tetraethylborate (NaBE₄, 1%, w/v) to react with 100 µL of acetate buffer (pH 4.9) on a cellulose filter (Millex® HA Filter, 0.45 µm) pre-soaked with MilliQ water for 20 minutes in the dark. The filter was then conditioned by purging the excess solution and passing Hg free air through the filter for 5 min at the sampling flow rate (i.e., 1 L min⁻¹).

The NaBE₄ solution was prepared in the laboratory at Trent University prior to the field sampling trip and kept frozen in the dark until use. Preliminary test in the laboratory revealed that the ethylating reagent could be stored for up to three months at -20°C in the dark without significant losses in efficiency.

During sampling, the conditioned ethylation filter was connected to the sampling set up (i.e., sodalime trap and collection traps in series) for preconcentration of methylated Hg species. No transformation was required for dimethylmercury (DMHg) collection.

The air stream was dried using a sodalime trap (∼ 2.5 g 4–8 mesh sodalime ACS, Alfa Aesar, in PTEFE tube) before entering the collection traps. Collection traps were made by packing borosilicate tubes (11.5 cm long, 0.40 cm ID) with Tenax® TA 20/35 (TA, Mandel Scientific, 0.1 g) or Bond Elut ENV (BE, Varian Inc., 0.1 g). Since BE is only available in small particle size (125 µm), wider tubes (0.7 cm ID) were used to minimize backpressure at a sampling flow rate of 1 L min⁻¹. Clean silanized glass wool was added at both ends of the tubes to retain the adsorbent firmly packed in the tube and prevent dragging during sampling and flushing. More information about collection traps preparation and conditioning is given in a previous article [15].
A sampling volume of 200 L was achieved during sampling by using collection traps in series (2 for BE and 4 for TA) and maintaining the traps at 4°C. After sampling, Hg species collected on individual traps were transferred onto a single analytical trap for further preconcentration. The analytical traps were capped at each end, doubled bagged and kept in air tight glass containers prior to and after sampling and stored in the dark at -20°C until analysis in the laboratory.

The online ethylation process was optimized in the laboratory prior to the sampling campaign. The % recovery of a known amount of MMHg loaded on Tenax® TA traps after ethylation was 89 ± 17.2 %.

Possible contamination or losses during the sampling campaign were assessed by determining MMHg and DMHg concentrations in travel blanks and storage standards. Storage standards consisted of a known concentration of MMHg preloaded on traps prior to the sampling campaign while the travel blanks were determined from clean traps from the same batch as collection trap that were opened and re-sealed during sampling on board the ship. The clean traps were stored together with the sample collection traps.

**Water sampling**

The glass bottles used for water sampling were first rinsed thoroughly with Milli-Q water. The bottles were then placed in a 5% (v/v) BrCl bath overnight at room temperature, thoroughly rinsed with MilliQ water and then transferred into a 10% (v/v) reagent grade HCl bath overnight at room temperature. Finally, the bottles were thoroughly rinsed with MilliQ water, filled to 25% volume with 1% reagent grade HCl, tightly capped and stored in double zipped bags until sampling. The bottles were also rinsed (3 times) with sample
water prior to water collection for analysis. Water was sampled according to recommended
protocols.

**Ancillary data and calculations**

Ancillary oceanographic data were obtained with a carousel water sampler (Sea-Bird 32,
Sea-Bird Electronics, Inc., Bellevue, WA, USA) equipped with a CTD (Conductivity,
Temperature, Depth) sensors to measure temperature and salinity (Sea-Bird 911plus, Sea-
Bird Electronics, Inc., Bellevue, WA, USA). Dissolved oxygen (Sea-Bird SBE43) and *in vivo*
fluorescence (SeaPoint Chlorophyll Fluorometer, Seapoint Sensors, Inc., Exeter, NH,
USA) were also measured. Chlorophyll *a* concentration and net primary production (PP)
rates were measured using the fluorometric method (Turner Designs 10-AU fluorometer,
Turner Designs, Sunnyvale, CA, USA) and the *14*C-uptake method, respectively. The
procedures are detailed elsewhere [16]. The surface mixed layer depth was determined as
the depth with maximum value of the Brunt-Väisälä (or buoyancy) frequency (N² in s⁻²),
which was estimated from the difference in seawater density between consecutive depth
intervals according to Pond and Pickard [17] using the following equation:

\[ N^2 = \frac{g}{\rho} \frac{d\rho}{dz} \]

where *g* (m s⁻²) is the gravitational acceleration, \( \rho \) (kg m⁻³) is the seawater density and *z*
(m) is the depth. N² is an indicator of stratification strength of the upper water column.

**Dissolved organic carbon (DOC) determination**
Each DOC water sample was filtered through precombusted (450°C for 5 h) Whatman GF/F filters. The filtrate was collected in 9 mL glass storage vials with Teflon-lined caps previously cleaned following the protocol of Burdige and Homstead [18] and acidified to ~pH 2 with 100 µl of 2 N HCl. The DOC samples were kept at 4°C in the dark until analysis (< 3 months). DOC was determined on a high-temperature combustion Shimadzu TOC-VCPN Total Organic Carbon Analyzer (Shimadzu Corporation, Kyoto, Japan) using the analysis procedure given in Whitehead et al [19]. Potassium hydrogen phthalate was used to standardize DOC measurements. In addition, samples were systematically checked against low carbon water (1 µmol L⁻¹) and deep seawater reference water (Florida Strait at 700 m; 41–44 µmol L⁻¹) every seventh sample analysis. These seawater DOC reference standards were produced by the Hansell’s Consensus Reference Materials (CRM) project (http://yyy.rsmas.miami.edu/groups/biogeochem/CRM.html). The mean DOC of three replicate injections of each water sample showed a typical coefficient of variation < 3%.
Figure A2 - 1. Schematic of sampling and preconcentration set up for methylated mercury species at the seawater - air interface over the ocean surface.
Figure A2 - 2. Sea conditions during air sampling in the Canadian Arctic on (a) 9 August 2010, (b) 7 August 2011, and (c) 9 August 2011.
Figure A2 - 3. Sea-ice coverage (%) in Hudson Bay (HB) in 2010 and the Canadian Arctic Archipelago regions in 2010 and 2011; Franklin strait / Coronation Gulf (Fran), Lancaster Sound (Lan), and eastern entrance of Lancaster Sound (Lan Mouth). The sampling periods are indicated by the shaded areas. Sea-ice coverage data from the Canadian Ice Service – Environment Canada (http://www.ec.gc.ca/glaces-ice/).
Figure A2 - 4. Average sea ice concentrations in the Arctic for (a) July and (b) August 2010 as well as (c) July and (d) August 2011. Image/photo courtesy of the National Snow and Ice Data Center, University of Colorado, Boulder (http://nsidc.org/data/nsidc-0081.html).
Figure A2 - 5. Dissolved organic carbon (DOC) concentration (averaged of a minimum of 4 samples collected in the upper 100 m of the water column or down to the bottom in shallow water) in Hudson Bay (HB) and the Canadian Arctic Archipelago (CAA) in mid-July to mid-August 2010 and 2011. Boxes extend from 25 to 75% quartiles with the middle line representing the median value; the whiskers extend from minimum to maximum values.
Figure A2 - 6. Hourly average incident downwelling photosynthetically available radiation (PAR) in Hudson Bay (HB) and the Canadian Arctic Archipelago (CAA) in mid-July to mid-August 2010 and 2011.
Table A2 - 1. Monomethylmercury (MMHg) and dimethylmercury (DMHg) concentrations at the seawater – air interface in Hudson Bay (HB) and the Canadian Arctic Archipelago (CAA) in summer 2010 and 2011. <LOD - below limit of quantification (0.015 pg m\(^{-3}\))

<table>
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<tr>
<th>Date</th>
<th>Sample</th>
<th>Latitude (N)</th>
<th>Longitude (W)</th>
<th>Region</th>
<th>Water Depth (m)</th>
<th>DMHg (pg m(^{-3}))</th>
<th>MMHg (pg m(^{-3}))</th>
<th>MMHg : DMHg (g : g)</th>
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<td>Longitude (W)</td>
<td>Region</td>
<td>Water Depth (m)</td>
<td>DMHg (pg m$^{-3}$)</td>
<td>MMHg (pg m$^{-3}$)</td>
<td>MMHg : DMHg (g : g)</td>
</tr>
<tr>
<td>------------</td>
<td>--------</td>
<td>--------------</td>
<td>---------------</td>
<td>--------</td>
<td>----------------</td>
<td>---------------------</td>
<td>--------------------</td>
<td>----------------------</td>
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<tr>
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<td>CAA</td>
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<tr>
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<td>CAA</td>
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<td>1.9</td>
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<tr>
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<td>B8</td>
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<td>90°43.025</td>
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<td>-</td>
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<tr>
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<td>96°09.829</td>
<td>CAA</td>
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<td>72°23.081</td>
<td>95°59.335</td>
<td>CAA</td>
<td>350</td>
<td>&lt; LOD</td>
<td>0.5</td>
<td>-</td>
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<tr>
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<td>71°18.000</td>
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<td>CAA</td>
<td>162</td>
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<td>-</td>
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<tr>
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<td>69°11.000</td>
<td>100°45.000</td>
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<td>0.4</td>
<td>0.2</td>
</tr>
<tr>
<td>09/08/2011</td>
<td>B15</td>
<td>68°54</td>
<td>101°46</td>
<td>CAA</td>
<td>109</td>
<td>5.5</td>
<td>0.6</td>
<td>0.1</td>
</tr>
<tr>
<td>09/08/2011</td>
<td>B16</td>
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<td>104°11.585</td>
<td>CAA</td>
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<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>10/08/2011</td>
<td>B17</td>
<td>68°56.000</td>
<td>107°02.000</td>
<td>CAA</td>
<td>109</td>
<td>2.5</td>
<td>&lt; LOD</td>
<td>-</td>
</tr>
<tr>
<td>10/08/2011</td>
<td>B18</td>
<td>68°26</td>
<td>110°48</td>
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<td>109</td>
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<td>&lt; LOD</td>
<td>-</td>
</tr>
<tr>
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<td>B19</td>
<td>69°52.000</td>
<td>99°28.000</td>
<td>CAA</td>
<td>78</td>
<td>3.7</td>
<td>0.2</td>
<td>0.1</td>
</tr>
</tbody>
</table>
Table A2 - 2. Pearson correlation coefficients between monomethylmercury (MMHg) and dimethylmercury (DMHg) in the atmosphere and meteorological and oceanographic variables. SST: sea surface temperature, SSS: sea surface salinity, DOC: dissolved organic carbon, $Z_{ML}$: surface mixed layer depth, Zeu: euphotic depth, PP – primary production rate, $T_{Air}$: air temperature, PAR: cumulative daily incident photosynthetically available radiation, SWR: cumulative daily short wave radiation, Daily wind speed: average daily wind speed, $Z_{SCM}$: subsurface chlorophyll maximum depth, Chl $a$: chlorophyll $a$ in surface water (i.e. 2 or 5 m).

ns: not significant, *$p < 0.05$, **$p < 0.01$, ***$p < 0.001$

<table>
<thead>
<tr>
<th></th>
<th>MMHg</th>
<th>DMHg</th>
</tr>
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<tbody>
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<td>SST</td>
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<td>ns</td>
</tr>
<tr>
<td>SSS</td>
<td>ns</td>
<td>ns</td>
</tr>
<tr>
<td>Ice Cover</td>
<td>ns</td>
<td>0.52 ***</td>
</tr>
<tr>
<td>Cloud cover</td>
<td>0.21 *</td>
<td>ns</td>
</tr>
<tr>
<td>Wind speed</td>
<td>ns</td>
<td>ns</td>
</tr>
<tr>
<td>DOC</td>
<td>0.43 **</td>
<td>0.34 *</td>
</tr>
<tr>
<td>$Z_{ML}$</td>
<td>ns</td>
<td>0.26 **</td>
</tr>
<tr>
<td>$Z_{eu}$</td>
<td>ns</td>
<td>ns</td>
</tr>
<tr>
<td>PP</td>
<td>ns</td>
<td>0.74 **</td>
</tr>
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<td>Depth</td>
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<td>ns</td>
</tr>
<tr>
<td>$T_{Air}$</td>
<td>ns</td>
<td>ns</td>
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<tr>
<td>PAR</td>
<td>ns</td>
<td>ns</td>
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<tr>
<td>SWR</td>
<td>ns</td>
<td>ns</td>
</tr>
<tr>
<td>Daily wind speed</td>
<td>ns</td>
<td>ns</td>
</tr>
<tr>
<td>Dissolved O2</td>
<td>ns</td>
<td>0.18 *</td>
</tr>
<tr>
<td>$Z_{SCM}$</td>
<td>0.35</td>
<td>ns</td>
</tr>
<tr>
<td>Chl $a$</td>
<td>ns</td>
<td>ns</td>
</tr>
<tr>
<td>pH</td>
<td>0.48 ***</td>
<td>ns</td>
</tr>
</tbody>
</table>
Table A2 - 3. Monomethylmercury (MMHg) wet deposition calculated from MMHg concentration (pg m\(^{-3}\)) in air (MMHg\(_{\text{Air}}\)) in Hudson Bay (HB) and the Canadian Arctic Archipelago (CAA).

<table>
<thead>
<tr>
<th>Region</th>
<th>MMHg(_{\text{Air}})^a (pg m(^{-3}))</th>
<th>H(^b)</th>
<th>Calculated MMHg(_{\text{aq}}) (ng L(^{-1}))</th>
<th>Summer precipitation (mm)</th>
<th>Summer MMHg deposition (ng m(^{-2}) d(^{-1}))</th>
<th>MMHg deposition (ng m(^{-2}) d(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>HB</td>
<td>$7.5 \pm 4.7$</td>
<td>$0.9 \times 10^{-5}$</td>
<td>$0.83 \pm 0.52$</td>
<td>225(^c)</td>
<td>188 ± 117.5</td>
<td>1.5 ± 0.96</td>
</tr>
<tr>
<td>CAA</td>
<td>$3.6 \pm 2.1$</td>
<td>$0.9 \times 10^{-5}$</td>
<td>$0.40 \pm 0.23$</td>
<td>93(^d)</td>
<td>37 ± 21.7</td>
<td>0.3 ± 0.18</td>
</tr>
</tbody>
</table>

\(^a\) MMHg\(_{\text{Air}}\), mean value ± 1 standard deviation (SD)

\(^b\) H is the dimensionless gas - aqueous distribution constant (MMHg (g) MMHg (aq)\(^{-1}\)) at 10°C from Iverfeld and Lindqvist (1982) [215].

\(^c\) Average precipitation (1944 - 2008) for summer months (June to September) from Environment Canada Hudson Bay station 4083323.

\(^d\) Average precipitation (1948 - 2011) for summer months (June to September) from Environment Canada Resolute station 2403500.

Source: [222]
Literature Cited


APPENDIX 3: SUPPORTING INFORMATION FOR “METHYLATION AND DEMETHYLATION OF MERCURY IN POLAR MARINE WATERS”

Methods

Monomethylmercury determination

Monomethylmercury in sea water samples was extracted from its matrix by water vapor distillation. An internal standard of isotope enriched monomethylmercury (CH3201HgCl) was added to the samples prior to distillation to correct for procedural losses. After distillation, the distilled methylmercury was derivatized to volatile ethylmethylmercury by aqueous-phase ethylation using sodium tetraethylborate (NaBEt₄). The volatile ethylmethylmercury compounds generated were purged onto a Tenax traps using Hg-free nitrogen gas. Determination of monomethylmercury was achieved by thermodesorption (245°C) liberation, separation onto a packed gas chromatographic column (15% OV-3 Chromosorb, mesh 60/80) heated to 110°C and detection of specific Hg isotopes by inductively coupled plasma mass spectrometry (ICP-MS, Varian Inc.). The measurement procedure and the scheme to calculate the specific isotopes concentrations is described in detail elsewhere [1].

The method detection limit for MMHg was 0.5 pgL⁻¹ with 50 ml of sample based on 3 standard deviations of the blanks. % RSD < 10% were considered acceptable with distillation blanks of < 1 pgL⁻¹.
**Dimethylmercury determination**

DMHg trapped on Carbotraps was liberated by thermodesorption and sent to a packed glass column (15% OV-3 Chromosorb, mesh 60/80) heated to 80°C for separation by gas chromatography (GC) and detection by inductively coupled plasma mass spectrometry (ICP-MS, Varian Inc.). The instrument, including the GC setup, was calibrated for mass response with known quantities of monomethylmercury, which were thermally desorbed from Tenax traps after derivatization by aqueous phase ethylation and purge and trap. DMHg standards were used for DMHg retention time determination and prepared by purging a known amount of DMHg from an aqueous solution and trapping on carbotraps which were subsequently desorbed and sent to the GC-ICP-MS for detection. The detection limit was 0.5 pg.

**Total mercury (THg) determination**

The exact concentration of the isotope enriched species (i.e. $^{200}$Hg$^{2+}$, CH$_3$$^{199}$Hg$^+$ and (CH$_3$)$_2$$^{198}$Hg) were determined as THg and quantified after bromine chloride (BrCl) oxidation, followed by reduction using tin chloride (SnCl$_2$) reduction, purging and trapping by gold-trap amalgamation and detection by inductively coupled plasma mass spectrometry (ICP-MS). THg concentration in BrCl solution was also determined and measured concentrations were corrected accordingly.

**Dissolved organic carbon (DOC) determination**

Each DOC water sample was filtered through precombusted (450°C for 5 h) Whatman GF/F filters. The filtrate was collected in 9 mL glass storage vials with Teflon-lined caps previously cleaned following the protocol of Burdige and Homstead (1994) [2] and
acidified to ~ pH 2 with 100 µl of 2 N HCl. The DOC samples were kept at 4°C in the dark until analysis (< 3 months). DOC was determined on a high-temperature combustion Shimadzu TOC-VCPN Total Organic Carbon Analyzer using the analysis procedure given in Whitehead et al. (2000) [3]. Potassium hydrogen phthalate was used to standardize DOC measurements. In addition, samples were systematically checked against low carbon water (1 µmol L\(^{-1}\)) and deep seawater reference water (Florida Strait at 700 m; 41–44 µmol L\(^{-1}\)) every seventh sample analysis. These seawater DOC reference standards were produced by the Hansell’s Consensus Reference Materials (CRM) project (http://yyy.rsmas.miami.edu/groups/biogeochem/CRM.html). The mean DOC of three replicate injections of each water sample showed a typical coefficient of variation < 3%. 
Table A3 - 1. Details on the stations sampled in Hudson Bay (2010) and the Canadian Arctic Archipelago (2011) for incubation experiments.

<table>
<thead>
<tr>
<th>Year</th>
<th>Date</th>
<th>Latitude (N)</th>
<th>Longitude (W)</th>
<th>Station</th>
<th>Sampling Depth (m)</th>
<th>Water column Depth (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2010</td>
<td>July-13-10</td>
<td>55°24.535</td>
<td>77°55.859</td>
<td>702</td>
<td>27</td>
<td>134</td>
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<tr>
<td>2010</td>
<td>July-19-10</td>
<td>59°58.165</td>
<td>91°57.051</td>
<td>707</td>
<td>50</td>
<td>101</td>
</tr>
<tr>
<td>2010</td>
<td>July-21-10</td>
<td>58°46.688</td>
<td>91°32.096</td>
<td>706</td>
<td>40</td>
<td>78</td>
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<tr>
<td>2010</td>
<td>July-23-10</td>
<td>57°26.501</td>
<td>91°54.550</td>
<td>705a</td>
<td>15</td>
<td>34</td>
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<tr>
<td>2010</td>
<td>July-24-10</td>
<td>57°40.210</td>
<td>91°36.194</td>
<td>705</td>
<td>14</td>
<td>64</td>
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<tr>
<td>2010</td>
<td>July-30-10</td>
<td>62°8.072</td>
<td>81°23.989</td>
<td>850</td>
<td>32</td>
<td>208</td>
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<tr>
<td>2011</td>
<td>July-28-11</td>
<td>70°17.657</td>
<td>66°5.692</td>
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<td>20</td>
<td>310</td>
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<td>2011</td>
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<td>72°40.354</td>
<td>78°34.865</td>
<td>160</td>
<td>25</td>
<td>700</td>
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<tr>
<td>2011</td>
<td>August-03-11</td>
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<td>26</td>
<td>115</td>
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<td>2011</td>
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<td>71°17.923</td>
<td>97°36.212</td>
<td>310</td>
<td>32</td>
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Table A3 - 2. Concentrations of isotope enriched mercury (Hg) species used to assess the production and loss of methylated Hg species in water. MM$^{199}$Hg: monomethylmercury, DM$^{198}$Hg: dimethylmercury, $^{200}$Hg$^{2+}$: inorganic Hg.

<table>
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<th>Experiment 1</th>
<th>Experiment 2</th>
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<td>MM$^{199}$Hg (pgL$^{-1}$)</td>
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<tr>
<td>DM$^{198}$Hg (pgL$^{-1}$)</td>
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<td>35</td>
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<tr>
<td>$^{200}$Hg$^{2+}$ (ngL$^{-1}$)</td>
<td>40</td>
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Table A3 - 3. Nutrients concentrations at the sampling depths (subsurface chlorophyll maximum ~ 30 m) of the different stations where methylation and demethylation experiments were conducted.

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<th>Station</th>
<th>Nitrite (uM)</th>
<th>Nitrate (uM)</th>
<th>Silicate (uM)</th>
<th>Phosphate (uM)</th>
<th>Ammonium (uM)</th>
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<tr>
<td>702</td>
<td>0.12</td>
<td>0.19</td>
<td>2.92</td>
<td>0.59</td>
<td>0.07</td>
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<td>707</td>
<td>0.26</td>
<td>3.41</td>
<td>7.75</td>
<td>1.03</td>
<td>0.08</td>
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<td>706</td>
<td>0.14</td>
<td>0.81</td>
<td>2.82</td>
<td>0.76</td>
<td>0.04</td>
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<td>705a</td>
<td>0.18</td>
<td>1.55</td>
<td>4.55</td>
<td>0.69</td>
<td>0.06</td>
</tr>
<tr>
<td>705</td>
<td>0.18</td>
<td>1.55</td>
<td>4.55</td>
<td>0.69</td>
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<td>705</td>
<td>0.18</td>
<td>1.55</td>
<td>4.55</td>
<td>0.69</td>
<td>0.06</td>
</tr>
<tr>
<td>850</td>
<td>0.13</td>
<td>4.16</td>
<td>6.63</td>
<td>0.94</td>
<td>na*</td>
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<tr>
<td>180b</td>
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<td>3.90</td>
<td>6.30</td>
<td>0.76</td>
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<tr>
<td>175</td>
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<td>12.21</td>
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<tr>
<td>160</td>
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<tr>
<td>310</td>
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<td>3.54</td>
<td>8.54</td>
<td>0.94</td>
<td>0.07</td>
</tr>
</tbody>
</table>

*not available
Table A3 - 4. Correlation coefficients (Spearman correlation analysis) for important parameters including monomethylmercury (MMHg), dimethylmercury (DMHg), MMHg methylation rate constants ($k_{m1}$), dimethylmercury demethylation rate constants ($k_{d2}$). DOC: dissolved organic content, Chl $a$: chlorophyll $a$, T: seawater temperature. Level of significance: *p < 0.1, **p < 0.05, ***p < 0.01

<table>
<thead>
<tr>
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<th>DMHg</th>
<th>$k_{d2}$</th>
<th>$k_{m1}$</th>
<th>T</th>
<th>Phosphate</th>
<th>Chl $a$</th>
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<td>$k_{d2}$</td>
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<td>-0.71</td>
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<td>$k_{m1}$</td>
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<td>-0.56</td>
<td>0.37</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T</td>
<td>-0.16</td>
<td>-0.54</td>
<td>0.11</td>
<td><strong>0.91</strong></td>
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<td></td>
<td></td>
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<tr>
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<td>0.23</td>
<td><strong>-0.76</strong></td>
<td><strong>-0.88</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chl $a$</td>
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<td><strong>0.96</strong></td>
<td>-0.58</td>
<td>-0.43</td>
<td>-0.43</td>
<td>0.3</td>
<td></td>
</tr>
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<td>-0.3</td>
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<td><strong>0.79</strong></td>
<td>0.47</td>
<td>-0.35</td>
<td>-0.19</td>
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</tbody>
</table>
Table A3 - 5. Component matrix extracted from a principal component analysis (PCA) for monomethylmercury (MMHg) and dimethylmercury (DMHg) production in Arctic surface waters. km1: MMHg methylation rate constant, kd2: dimethylmercury demethylation rate constant. DOC: dissolved organic content, Chl a: chlorophyll a, T: seawater temperature. Component loadings > 0.6 are in bold.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Component</th>
<th>1</th>
<th>2</th>
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<tbody>
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<td>MMHg</td>
<td></td>
<td>0.314</td>
<td>0.906</td>
</tr>
<tr>
<td>DMHg</td>
<td></td>
<td>-0.866</td>
<td>-0.338</td>
</tr>
<tr>
<td>(k_{d2})</td>
<td></td>
<td>0.638</td>
<td>0.713</td>
</tr>
<tr>
<td>(k_{m1})</td>
<td></td>
<td>0.893</td>
<td>-0.362</td>
</tr>
<tr>
<td>T</td>
<td></td>
<td>0.797</td>
<td>-0.524</td>
</tr>
<tr>
<td>Phosphate</td>
<td></td>
<td>-0.579</td>
<td>0.795</td>
</tr>
<tr>
<td>Chl a</td>
<td></td>
<td>-0.768</td>
<td>-0.302</td>
</tr>
<tr>
<td>DOC</td>
<td></td>
<td>0.675</td>
<td>-0.094</td>
</tr>
<tr>
<td>% of variance</td>
<td></td>
<td>50.8</td>
<td>32.3</td>
</tr>
<tr>
<td>Cumulative variance</td>
<td></td>
<td>50.8</td>
<td>83.1</td>
</tr>
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Stn 160
Figure A3 - 1. Chemical and biological parameters throughout the water column at the stations sampled during the ArcticNet 2010 (stations 702, 707, 706, 705a, 705 and 850) and ArcticNet 2011 (Stations 175, 160, 331 and 310) expeditions of board *CCGS Amundsen* in Hudson Bay and the Canadian Arctic Archipelago respectively. The grey horizontal lines the sampling depths at each station.
Figure A3 - 2. Relationship between MMHg demethylation rate constant (kd1amb, d-1) and MMHg concentrations in Arctic and subarctic surface waters.
Figure A3 - 3. Relationship between concentrations of (a) ambient monomethylmercury (MMHg) and newly produced MM$^{200}$Hg (from $^{200}$Hg(II) spikes) and (b) % MM$^{200}$Hg produced from $^{200}$Hg(II) (MM$^{200}$Hg/$^{200}$Hg(II)) and dissolved organic (DOC) concentrations in Arctic and subarctic surface waters after 24 hours incubation.
Figure A3 - 4. Relationship between ambient dimethylmercury (DMHg) concentrations and size fractionated (a) chlorophyll *a* (Chl *a*) concentrations and primary productivity for water samples at the subsurface chlorophyll maximum in Hudson Bay (2010) and the Canadian Arctic Archipelago (2011) in summer (July – August). Nano: large phytoplankton (≥5 μm). Pico: small phytoplankton (0.7–5 μm).
Figure A3 - 5. Relationship between MMHg concentrations and DMHg demethylation rate constant (kd2, d\(^{-1}\)) in Arctic and subarctic surface waters.
Literature Cited

