

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/269036853>

Determination of Monomethylmercury and Dimethylmercury in the Arctic Marine Boundary Layer

ARTICLE in ENVIRONMENTAL SCIENCE AND TECHNOLOGY · JANUARY 2015

Impact Factor: 5.33 · DOI: 10.1021/es502601z

CITATIONS

6

READS

147

5 AUTHORS, INCLUDING:



Pascale Anabelle Baya

Paul Sabatier University - Toulouse III

8 PUBLICATIONS 25 CITATIONS

SEE PROFILE



Michel Gosselin

Université du Québec à Rimouski UQAR

184 PUBLICATIONS 5,355 CITATIONS

SEE PROFILE



Igor Lehnher

University of Toronto

47 PUBLICATIONS 451 CITATIONS

SEE PROFILE



Holger Hintelmann

Trent University

142 PUBLICATIONS 4,609 CITATIONS

SEE PROFILE

Determination of Monomethylmercury and Dimethylmercury in the Arctic Marine Boundary Layer

Pascale A. Baya,^{*,†} Michel Gosselin,[‡] Igor Lehnher,[§] Vincent L. St.Louis,^{||} and Holger Hintelmann[⊥]

[†]Environmental & Life Sciences Graduate Program, Trent University, 1600 West Bank Drive, Peterborough, Ontario, K9J 7B8, Canada

[‡]Institut des sciences de la mer, Université du Québec à Rimouski, 310 Allée des Ursulines, Rimouski, Québec G5L 3A1, Canada

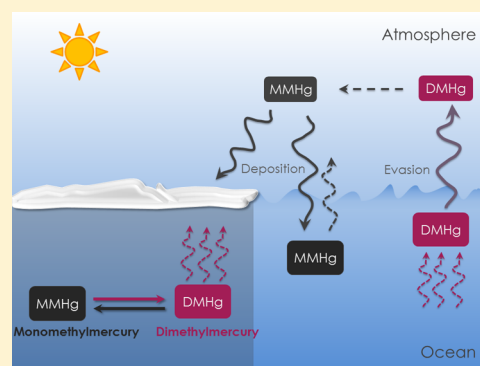
[§]Department of Geography, University of Toronto-Mississauga, 3359 Mississauga Rd, Mississauga, Ontario L5L 1C6, Canada

^{||}Department of Biological Sciences, University of Alberta, 116 St and 85 Ave, Edmonton, Alberta T6G 2E9, Canada

[⊥]Water Quality Centre, Trent University, 1600 West Bank Drive, Peterborough, Ontario, K9J 7B8, Canada

S Supporting Information

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. Overall atmospheric MMHg and DMHg concentrations (mean \pm SD) were 2.9 ± 3.6 and 3.8 ± 3.1 ($n = 37$) pg m⁻³, respectively. Concentrations of methylated Hg species in the marine boundary layer varied significantly among 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 Canadian Arctic 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 biomagnification in the pelagic food web.



1. 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 regions⁴ 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 bioaccumulative form of Hg and constitutes the majority (>75%) of Hg present in marine animals.^{7,8} 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, for example, 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.^{9,17} 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, CH₃HgCl) 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.

Received: May 28, 2014

Revised: November 26, 2014

Accepted: December 1, 2014

Published: December 1, 2014

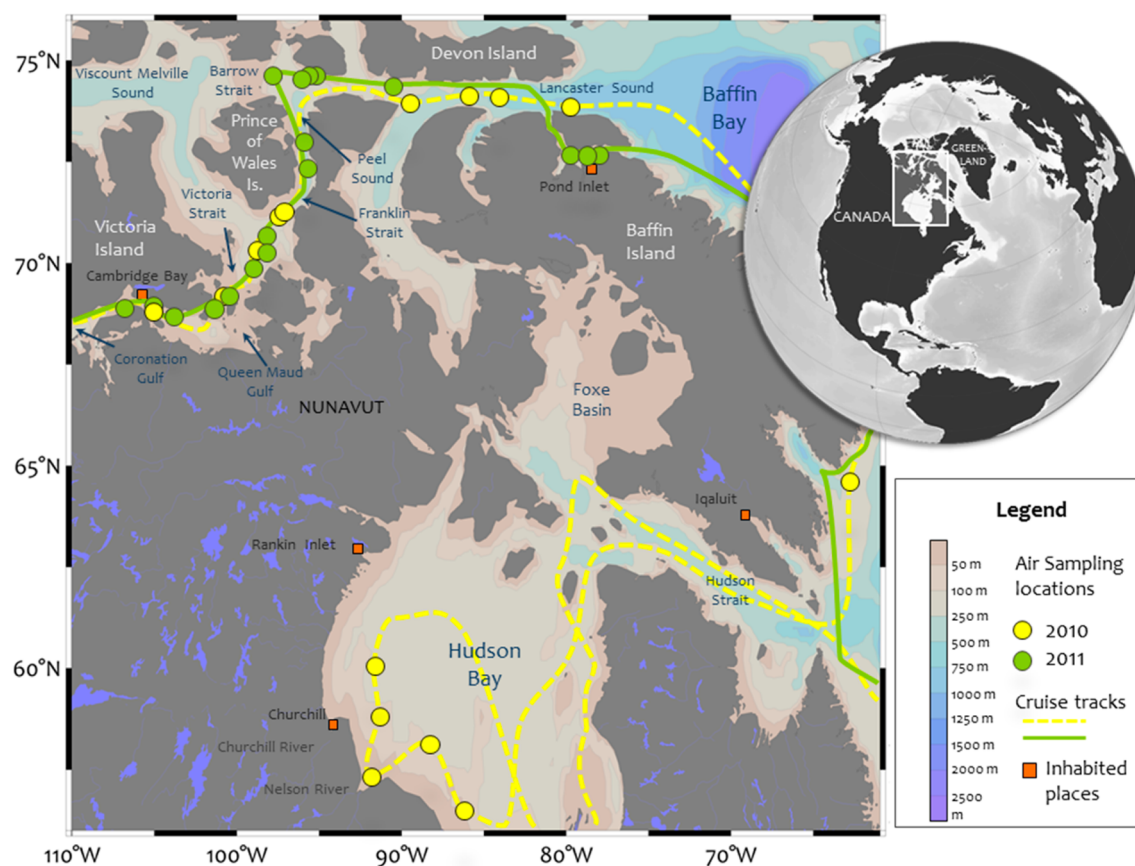


Figure 1. Map of the study area showing the cruise tracks and air sampling locations for methylated Hg species (monomethylmercury, MMHg and dimethylmercury DMHg) determination in 2010 (yellow circle) and 2011 (green circle). See Table 1 for site characteristics.

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.

2. MATERIALS AND METHODS

2.1. 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 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, Victoria 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 1. A description of the study area is given in the SI.

2.2. 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.

2.2.1. 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 inlet 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 h^{−1}) under headwind conditions (wind direction of 60°E and 60°W relative to direction of travel) and moderate absolute wind speed (≤10 m s^{−1}) to minimize interferences and contamination from the ship (see the SI for additional details).

2.2.2. 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 - NaBEt₄, 1%

Table 1. Environmental and Biological Variables (Mean \pm SD) in Hudson Bay (HB) and Canadian Arctic Archipelago (CAA) during Air Sampling Period (July–August 2010 and 2011)^a

	HB 2010	CAA 2010	CAA 2011
air temperature (°C)	9 \pm 4.5*	4 \pm 2.9	6 \pm 2.7
relative humidity (%)	96 \pm 6.1	93 \pm 4.4	92 \pm 5.4
sea surface temperature (°C)	5 \pm 2.8**	3 \pm 2.5	3 \pm 1.2
sea surface salinity (psu)	28 \pm 1.8	28 \pm 1.8	26 \pm 4.5
PAR (μ mol photons m ⁻² s ⁻¹) ^a	446 \pm 539	381 \pm 450	375 \pm 367
wind speed (m s ⁻¹) ^a	3.4 \pm 1.44	3.6 \pm 0.92	3.4 \pm 1.42
ice cover (%) ^b	0*	17 \pm 9	5 \pm 6
cloud cover (%) ^b	30 \pm 26**	70 \pm 20	66 \pm 27
water depth (m)	82 \pm 51	269 \pm 234	222 \pm 197
mixed layer depth (m)	12 \pm 6	10 \pm 5	11 \pm 7.5
SCM depth (m) ^c	30 \pm 10	27 \pm 5	29 \pm 14
DOC (μ mol L ⁻¹) ^d	104 \pm 12.8 (10)***	72 \pm 3.9 (5)	69 \pm 3.5 (8)
PP (mg C m ⁻² d ⁻¹) ^e	395 \pm 265 (6)	1072 \pm 711 (4)	734 \pm 663 (7)

^aWind 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 (SSM/I/S) from the National Snow and Ice Data Center (NSIDC)). ^cSCM, subsurface chlorophyll maximum. ^dDOC, Dissolved organic carbon, integrated over 100 m or bottom depth if shallower and divided by the integration depth. ^ePP, 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 parentheses, (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* \leq 0.05, ***p* \leq 0.01, ****p* \leq 0.001.

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 SI.

2.2.1. 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 airtight 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 SI Figure S1, 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 $89 \pm 17.2\%$. The limit of quantification (LOQ) calculated as ten times the standard deviation of bubbler blank (10 SD_{bubbler blank}) used for standards, was 0.5 pg whereas the limit of detection (LOD, 3 SD_{bubbler blank}) 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* > 0.05) was observed from the standard traps, during the storage period of three months.

2.3. 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.^{9,30} Water samples were collected at one location along each air sampling route (which extended 50–70 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/MS³¹ (see the SI for additional details).

2.4. Ancillary Data and Calculations. Vertical profiles of oceanographic variables such as temperature, salinity, dissolved oxygen, and in vivo fluorescence were measured using 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 seven 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 SI.

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.³²

Daily sea-ice concentrations were estimated from satellite imagery (F17 special sensor microwave imager (SSM/I/S); ~ 25 km spatial resolution) obtained from the F17 special sensor microwave imager (SSM/I/S) by the National Snow and Ice Data Center (NSIDC).³³

3. RESULTS AND DISCUSSION

3.1. Biogeochemical Characteristics of Study Area. The water column depths at sampling locations ranged from 35 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 (SI Table S1). 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

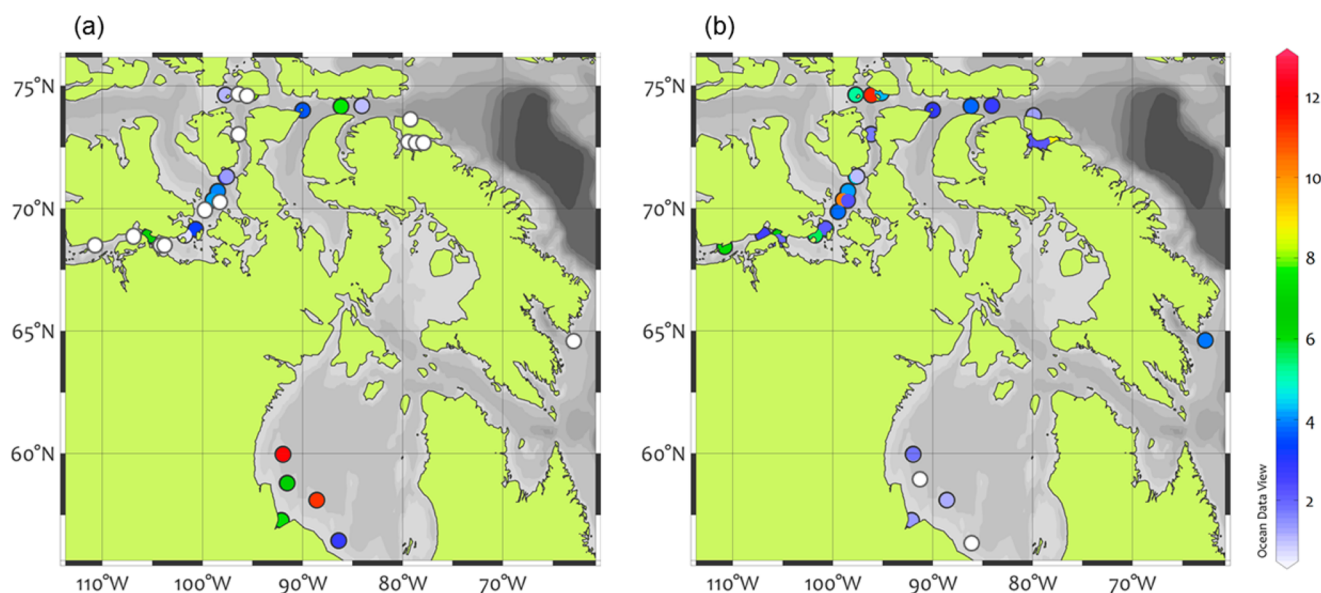


Figure 2. Spatial distribution of (a) monomethylmercury (MMHg) and (b) dimethylmercury (DMHg), in pg m^{-3} , in Hudson Bay and the Canadian Arctic Archipelago marine boundary layer in summer (mid-July to mid-August). Concentrations below the method detection limit ($<0.5 \text{ pg m}^{-3}$) are in white.

incident PAR was observed in HB while PP was higher in the CAA (Table 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 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 (SI Figure S3). The different sea conditions encountered during sampling campaigns are shown in SI Figure S2 and other environmental characteristics of the HB and CAA regions are given in Table 1.

3.2. 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 2). MMHg concentrations were below the LOQ ($<0.5 \text{ pg m}^{-3}$) during 16 of the 37 sampling events and these nondetect 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 $< \text{LOQ}$ during 4 sampling events only (SI Table S1). 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 among the sites (Figure 3b and Table 2). For example, MMHg concentrations were significantly (t -test, $p \leq 0.01$) higher over HB ($7.5 \pm 4.7 \text{ pg m}^{-3}$) than over the CAA

($3.6 \pm 2.1 \text{ pg m}^{-3}$ and $0.8 \pm 1.7 \text{ pg m}^{-3}$ for 2010 and 2011, respectively) whereas DMHg concentrations were significantly (t -test, $p \leq 0.01$) higher over the CAA ($5.4 \pm 2.9 \text{ pg m}^{-3}$ and $3.7 \pm 3.2 \text{ pg m}^{-3}$ for 2010 and 2011, respectively) than over HB ($1.3 \pm 1.2 \text{ pg m}^{-3}$). 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 ($\pm 1 \text{ SD}$) MMHg and DMHg concentrations in the Arctic MBL at all sites were 2.9 ± 3.6 ($n = 37$) and 3.8 ± 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 2 and Table 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: $5\text{--}97 \text{ pg m}^{-3}$) 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}

Based on previous reports of reactive gaseous mercury (RGM) concentrations (mean 30.1 pg m^{-3} , range $3.5\text{--}105.4 \text{ pg m}^{-3}$) over Arctic sea-ice,³⁴ our results suggest that even though methylated Hg species represent only a minor ($\sim 1\%$) fraction of the total atmospheric gaseous Hg pool, MMHg may constitute up to 25% of RGM in the Arctic MBL.

3.3. 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 2) are consistent with previously reported values for Arctic marine waters,^{5,9,10} as

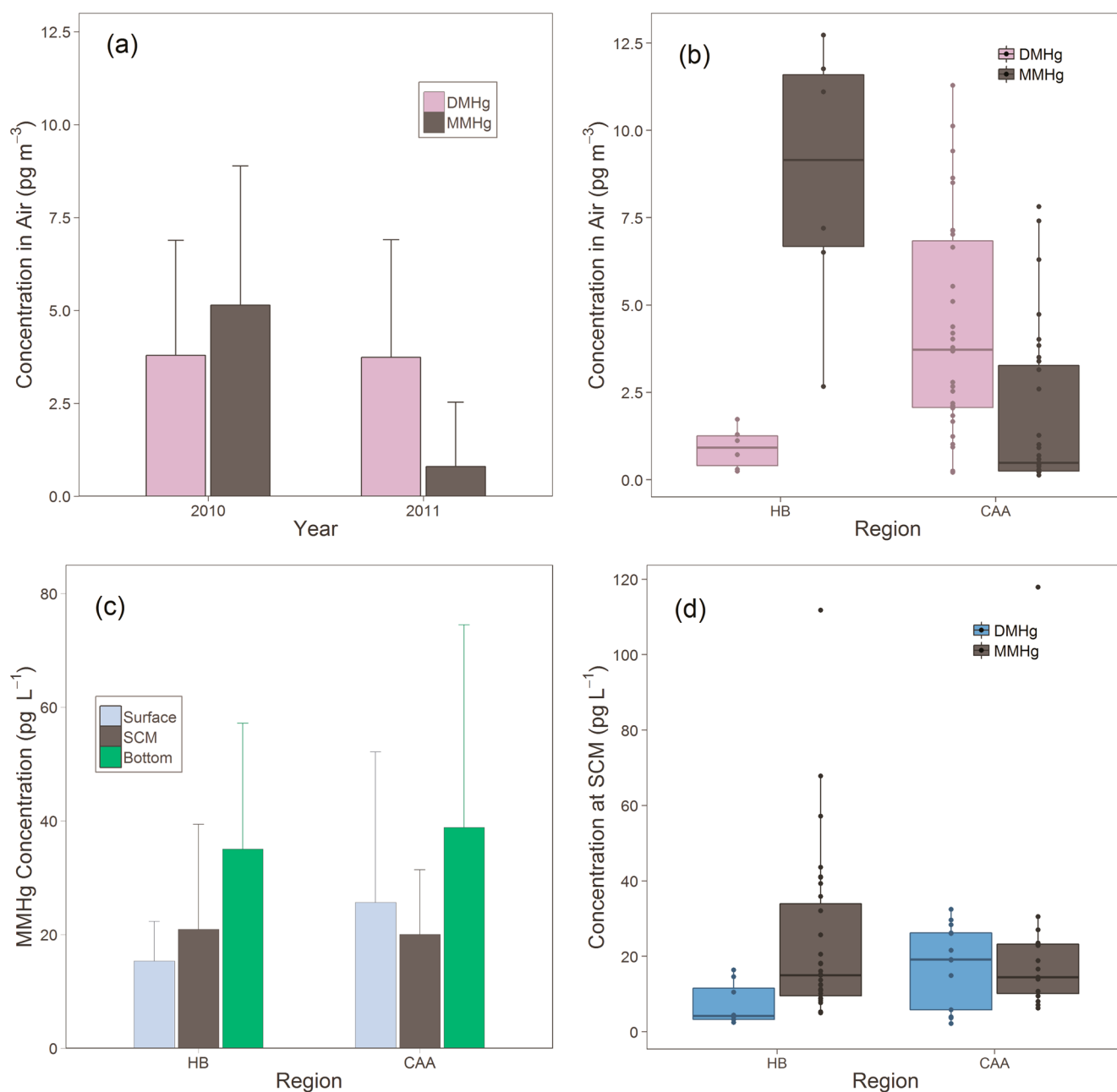


Figure 3. Monomethylmercury (MMHg) and dimethylmercury (DMHg) concentrations in the Arctic marine boundary layer (a) averaged for 2010 and 2011 and (b) for Hudson Bay (HB) and the Canadian Arctic Archipelago (CAA). Methylated air concentrations in 2010 are from HB and CAA while those for 2011 are from 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.

well as for Pacific,³⁵ Equatorial Pacific,²¹ Northern Atlantic³⁶ and Mediterranean³⁷ 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 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 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 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).

Table 2. Concentrations of Monomethylmercury (MMHg) and Dimethylmercury (DMHg) 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^a

	2010		2011	
	MMHg	DMHg	MMHg	DMHg
Air				
HB	7.5 \pm 4.7 (7)	1.3 \pm 1.2 (7)		
CAA	3.6 \pm 2.1 (11)	5.4 \pm 2.9 (11)	0.8 \pm 1.7 (19)	3.7 \pm 3.2 (19)
Seawater Surface				
HB	15.3 \pm 6.96 (11)			
CAA	17.6 \pm 5.16 (5)	6.8 \pm 6.0 (5)	25.7 \pm 26.43 (10)	3.4 \pm 1.96 (7)
Subsurface Chlorophyll Maximum (SCM)				
HB	20.9 \pm 18.46 (11)	5.6 \pm 4.12 (3)		
CAA	16.7 \pm 2.05 (5)	24.3 \pm 5.02 (5)	20.1 \pm 11.35 (7)	13.0 \pm 7.98 (5)
Bottom				
HB	35.0 \pm 22.12 (11)			
CAA	27.2 \pm 18.9 (5)	31.0 \pm 10.52 (3)	38.8 \pm 35.67 (7)	

^aMean values \pm SD are shown. The sample size is given in parentheses, (*n*). A value of 0.25 pg m^{-3} ($0.5 \times \text{LOQ}$) was assigned to air samples with concentrations less than the limit of detection (LOD). See SI Table S1.

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 2) show a depletion of DMHg at the surface. This is presumably a result of DMHg 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.

3.4. DMHg and MMHg Interactions in Air. Since both DMHg and some volatile complexes of MMHg (e.g., $\text{CH}_3\text{HgCl}^{20}$) 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 the latter has lower solubility in seawater and much higher volatility (gas–aqueous distribution constant, $H = 0.31$ at 25°C)³⁸ than MMHg chloride complexes ($H = 1.9 \times 10^{-5}$ at 25°C).³⁹ 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 radicals⁴⁰ and chlorine atoms.⁴¹ 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 and coastal landscapes. It has been suggested that the DMHg residence time in the atmosphere is less than 1 day, and as such, high DMHg concentrations should be recorded close to its sources only.⁴²

3.4.1. Sources of DMHg in the MBL. High concentrations of both MMHg and DMHg were recorded at specific locations in the CAA MBL (i.e., at stations in western Lancaster Sound, Franklin Strait and Coronation Gulf, Figure 2). It is noteworthy that sea-ice was still present at the time of sampling (up to 30%, SI Figure S2–S4). Sea-ice cover reduces ocean–atmosphere exchange, and limits the photodegradation of methylated Hg species in the underlying surface water because ultraviolet radiation is attenuated as it passes through snow and sea-ice.^{43,44} The statistically significant positive relationship ($r^2 = 0.52$, $p < 0.001$) observed between DMHg concentrations in the MBL and % ice cover, shown in Figure 4a, suggests that sea-ice cover might control the volatilization of DMHg from ocean surface water by acting as a physical barrier. We posit that DMHg accumulates under sea-ice and rapidly evades to the atmosphere as the ice begins to break up. 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 3b, d), were also the regions in the Arctic with the highest PP due to the supply of nutrients from intense mixing.⁴⁵ Hg methylation occurring in oxic seawater has been linked to microorganism abundance and activity^{6,46} while higher DMHg production has previously been observed in highly productive zones.⁴⁷ 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 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.

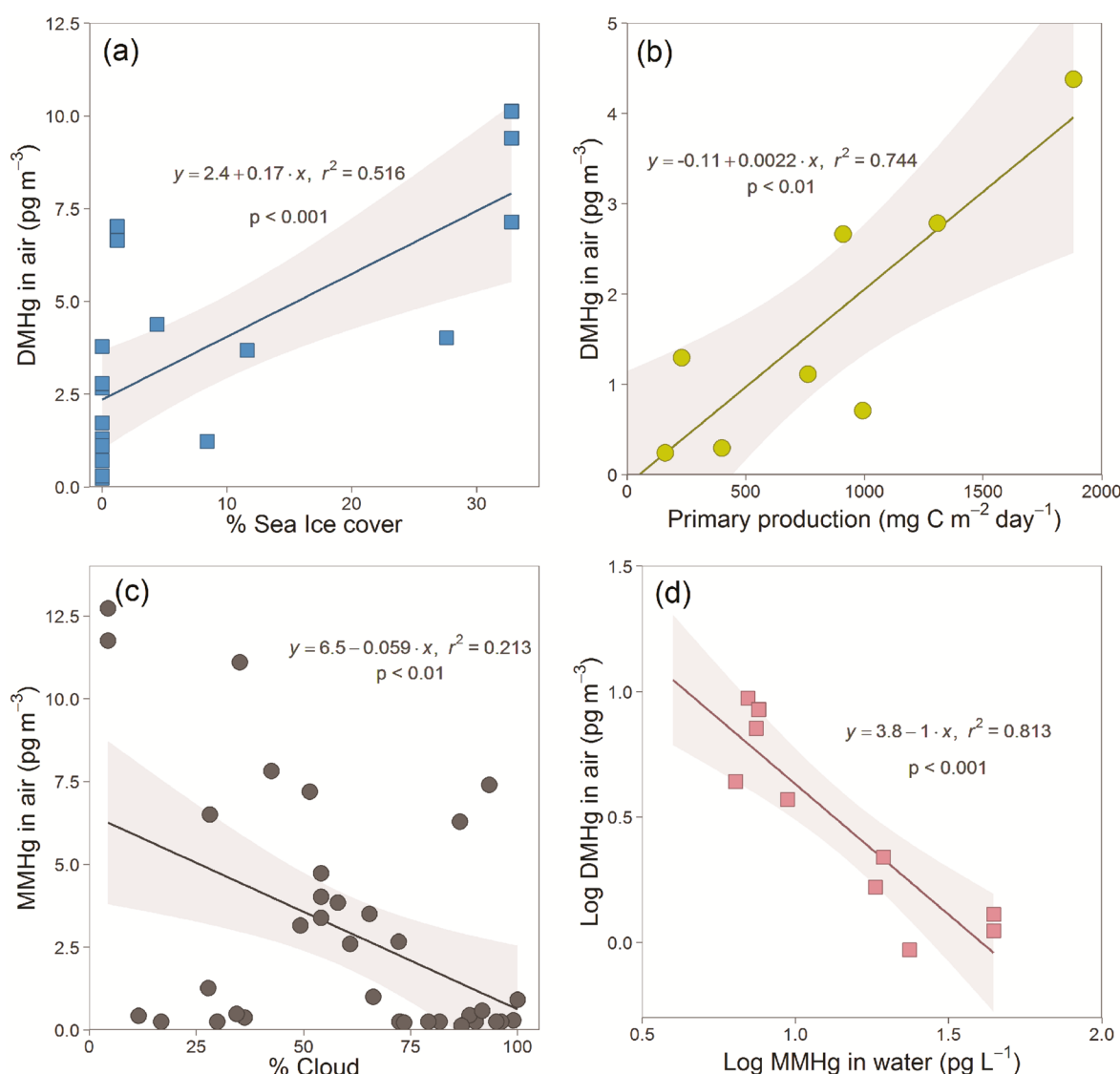


Figure 4. Relationships between (a) dimethylmercury (DMHg) concentrations in the Arctic marine boundary layer (MBL) and % ice cover at time of sampling in HB and the Canadian Arctic Archipelago in 2010 ($n = 17$, 95% slope confidence interval (CI) = 0.08 to 0.26), (b) DMHg concentrations in the MBL and 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 concentrations in the MBL and MMHg concentrations in surface seawater ($n = 10$, CI = -1.45 to -0.63). Lines plotted represent a linear regression. Level of significance: $p \leq 0.05$.

3.4.2. 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 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,⁴⁸ this observation suggests that in addition to radiation intensity, light spectral distribution influences the extent of DMHg photodegradation to MMHg in the MBL.

Light driven reactions would be more prevalent in HB, where radiation intensity and amplitude is higher (SI Figure S6), than in the CAA because it is located at lower latitude. HB is also characterized by relatively higher DOC concentration in water (Table 1 and SI Figure S5). 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 statistically 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 SI Table S2). This lack of relation is however not surprising and is explained by the air sampling time resolution (3 h), which was too low to capture a response to fast changing conditions (e.g., demethylation of DMHg or 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.

3.5. 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 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 statistically significant negative relationship between DMHg concentrations in air and MMHg in surface water (Figure 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 0.9×10^{-5} ,³⁹ the calculated concentrations of MMHg in precipitation for HB and CAA are $0.83 \pm 0.52 \text{ ng L}^{-1}$ and $0.4 \pm 0.23 \text{ ng L}^{-1}$, respectively (SI Table S3). These predicted concentrations are higher but not inconsistent with those measured in Arctic precipitation (<0.008 – 0.18 ng L^{-1})⁴⁹ 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}),⁵⁰ boreal precipitation (0.07 – 0.31 ng L^{-1})⁵¹ as well as Californian Coast precipitation (rain: $0.1 \pm 0.04 \text{ ng L}^{-1}$ and fog: $3.4 \pm 3.8 \text{ ng L}^{-1}$).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/>⁵²), we estimate that average June to August MMHg wet deposition is $188 \pm 117.5 \text{ ng m}^{-2}$ and $37 \pm 21.7 \text{ ng m}^{-2}$ in these two regions (SI Table S3). These wet deposition rates of $1.5 \pm 0.96 \text{ ng m}^{-2} \text{ d}^{-1}$ and $0.3 \pm 0.18 \text{ ng m}^{-2} \text{ d}^{-1}$ for HB and the CAA represent a small portion of previously reported DMHg evasion flux estimates for HB and CAA ($16.9 \text{ ng m}^{-2} \text{ d}^{-1}$ and $40 \text{ ng m}^{-2} \text{ d}^{-1}$, 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 ($>1 \text{ cm s}^{-1}$).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/>)⁵³ 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.

■ ASSOCIATED CONTENT

Supporting Information

Supporting Information available: Detailed procedure, additional figures and tables. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: pascalbaya@trentu.ca.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research was funded by the Network of Centres of Excellence of Canada, ArcticNet and the Natural Sciences and Engineering Research Council (NSERC) of Canada. We also like to acknowledge partial funding from Aboriginal Affairs and Northern Development Canada's Northern Contaminants Program. We thank the captains, officers and crews of the CCGS Amundsen and ArcticNet staff for their outstanding logistic support and field work assistance. We are grateful to Brent Else and Tim Papakyriakou (CEOS, University of Manitoba) for the meteorological data; Yves Gratton (INRS-ETE) and Pascal Guillot (UQAR) for the CTD data; Marjolaine Blais, Joannie Ferland and Mathieu Ardyna (UQAR) for assistance in the field and laboratory; Mélanie Simard for DOC analysis; and Drs. Dennis A. Hansell and Wenhao Chen (Rosenstiel School of Marine & Atmosphere Science, Division of Marine and Atmospheric Chemistry, University of Miami, Miami, Florida) for providing the DOC Consensus Reference Materials. Special thanks to Mathieu Ardyna (Université Laval) for compiling the sea-ice concentrations data and his very insightful comments. P.A.B. is especially grateful to Connie Lovejoy (Université Laval) for providing the stimulating working environment during the writing of the manuscript.

REFERENCES

- (1) Selin, N. E. Global biogeochemical cycling of mercury: A review. *Annu. Rev. Env. Resour.* **2009**, *34*, 43–63.
- (2) Mason, R. P.; Sheu, G.-R. Role of the ocean in the global mercury cycle. *Global Biogeochem. Cycles* **2002**, *16*, GB1093.
- (3) Strode, S. A.; Jaeglé, L.; Selin, N. E.; Jacob, D. J.; Park, R. J.; Yantosca, R. M.; Mason, R. P.; Slemr, F. Air-sea exchange in the global mercury cycle. *Global Biogeochem. Cycles* **2007**, *21*, GB1017.
- (4) Lindberg, S.; Bullock, R.; Ebinghaus, R.; Engstrom, D.; Feng, X.; Fitzgerald, W.; Pirrone, N.; Prestbo, E.; Seigneur, C. A synthesis of progress and uncertainties in attributing the sources of mercury in deposition. *Ambio* **2007**, *36*, 19–33.
- (5) Lehnher, I.; St Louis, V. L.; Hintelmann, H.; Kirk, J. L. Methylation of inorganic mercury in polar marine waters. *Nat. Geosci.* **2011**, *4*, 298–302.
- (6) Monperrus, M.; Tessier, E.; Amouroux, D.; Leynaert, A.; Huonnic, P.; Donard, O. F. X. Mercury methylation, demethylation and reduction rates in coastal and marine surface waters of the Mediterranean Sea. *Mar. Chem.* **2007**, *107*, 49–63.
- (7) Campbell, L. M.; Norstrom, R. J.; Hobson, K. A.; Muir, D. C.; Backus, S.; Fisk, A. T. Mercury and other trace elements in a pelagic Arctic marine food web (Northwater Polynya, Baffin Bay). *Sci. Total Environ.* **2005**, *351*, 247–263.
- (8) *Assessment 2011: Mercury in the Arctic*; AMAP: Oslo, Norway, 2011; p xiv–193.
- (9) St. Louis, V. L.; Hintelmann, H.; Graydon, J. A.; Kirk, J. L.; Barker, J.; Dimock, B.; Sharp, M. J.; Lehnher, I. Methylated mercury species in Canadian High Arctic marine surface waters and snowpacks. *Environ. Sci. Technol.* **2007**, *41*, 6433–6441.
- (10) Kirk, J. L.; Louis, V. L. S.; Hintelmann, H.; Lehnher, I.; Else, B.; Poissant, L. Methylated mercury species in marine waters of the Canadian High and Sub Arctic. *Environ. Sci. Technol.* **2008**, *42*, 8367–8373.
- (11) Wang, F.; Macdonald, R. W.; Armstrong, D. A.; Stern, G. A. Total and methylated mercury in the Beaufort Sea: The role of local and recent organic remineralization. *Environ. Sci. Technol.* **2012**, *46*, 11821–11828.
- (12) Cossa, D.; Averty, B.; Pirrone, N. The origin of methylmercury in open Mediterranean waters. *Limnol. Oceanogr.* **2009**, *54*, 837–844.
- (13) Mason, R. P.; Choi, A. L.; Fitzgerald, W. F.; Hammerschmidt, C. R.; Lamborg, C. H.; Soerensen, A. L.; Sunderland, E. M. Mercury biogeochemical cycling in the ocean and policy implications. *Environ. Res.* **2012**, *119*, 101–117.
- (14) Sunderland, E. M.; Krabbenhoft, D. P.; Moreau, J. W.; Strode, S. A.; Landing, W. M. Mercury sources, distribution, and bioavailability in the North Pacific Ocean: Insights from data and models. *Global Biogeochem. Cycles* **2009**, *23*, GB2010.
- (15) Conaway, C. H.; Black, F. J.; Weiss-Penzias, P.; Gault-Ringold, M.; Flegal, A. R. Mercury speciation in Pacific coastal rainwater, Monterey Bay, California. *Atmos. Environ.* **2010**, *44*, 1788–1797.
- (16) Weiss-Penzias, P. S.; Ortiz, C., Jr.; Acosta, R. P.; Heim, W.; Ryan, J. P.; Fernandez, D.; Collett, J. L., Jr.; Flegal, A. R. Total and monomethyl mercury in fog water from the central California coast. *Geophys. Res. Lett.* **2012**, *39*, L03804.
- (17) St Louis, V. L.; Sharp, M. J.; Steffen, A.; May, A.; Barker, J.; Kirk, J. L.; Kelly, D. J. A.; Arnott, S. E.; Keatley, B.; Smol, J. P. Some sources and sinks of monomethyl and inorganic mercury on Ellesmere Island in the Canadian High Arctic. *Environ. Sci. Technol.* **2005**, *39*, 2686–2701.
- (18) Gardfeldt, K.; Munthe, J.; Stromberg, D.; Lindqvist, O. A kinetic study on the abiotic methylation of divalent mercury in the aqueous phase. *Environ. Sci. Technol.* **2003**, *304*, 127–36.
- (19) Hintelmann, H. Organomercurials. Their formation and pathways in the environment. *Met ions in life sciences* **2010**, 365.
- (20) Mester, Z.; Sturgeon, R. E. Detection of volatile organometal chloride species in model atmosphere above seawater and sediment. *Environ. Sci. Technol.* **2002**, *36*, 1198–201.
- (21) Mason, R. P.; Fitzgerald, W. F. Alkylmercury species in the equatorial Pacific. *Nature* **1990**, *347*, 457–459.
- (22) Lee, Y. H.; Wangberg, I.; Munthe, J. Sampling and analysis of gas-phase methylmercury in ambient air. *Environ. Sci. Technol.* **2003**, *304* (1–3), 107–13.
- (23) Brosset, C.; Lord, E. Methylmercury in ambient air. Method of determination and some measurement results. *Water, Air, Soil Pollut.* **1995**, *82*, 739–750.
- (24) Lindberg, S. E.; Southworth, G.; Prestbo, E. M.; Wallschläger, D.; Bogle, M. A.; Price, J. Gaseous methyl- and inorganic mercury in landfill gas from landfills in Florida, Minnesota, Delaware, and California. *Atmos. Environ.* **2005**, *39*, 249–258.
- (25) Pongratz, R.; Heumann, K. Production of methylated mercury and lead by polar macroalgae—a significant natural source for atmospheric heavy metals in clean room compartments. *Chemosphere* **1998**, *36*, 1935–1946.
- (26) Baya, P. A.; Hollinsworth, J. L.; Hintelmann, H. Evaluation and optimization of solid adsorbents for the sampling of gaseous methylated mercury species. *Anal. Chim. Acta* **2013**, *786*, 61–69.
- (27) Schroeder, W. H. Sampling and analysis of mercury and its compounds in the atmosphere. *Environ. Sci. Technol.* **1982**, *16*, A394–A400.
- (28) Larsson, T.; Bjorn, E.; Frech, W. Species specific isotope dilution with on line derivatisation for determination of gaseous mercury species. *J. Anal. Atom Spectrom.* **2005**, *20*, 1232–1239.
- (29) Hintelmann, H.; Evans, R. D.; Villeneuve, J. Y. Measurement of mercury methylation in sediments by using enriched stable mercury isotopes combined with methylmercury determination by gas-chromatography inductively-coupled plasma-mass spectrometry. *J. Anal. Atom Spectrom.* **1995**, *10*, 619–624.
- (30) Gill, G. A.; Fitzgerald, W. F. Mercury sampling of open ocean waters at the picomolar level. *Deep-Sea Res. Pt. A. Oceanographic Research Papers* **1985**, *32*, 287–297.
- (31) Hintelmann, H.; Evans, R. D. Application of stable isotopes in environmental tracer studies – Measurement of monomethylmercury

(CH₃Hg⁺) by isotope dilution ICP-MS and detection of species transformation. *Fresenius J. Anal. Chem.* **1997**, 358, 378–385.

(32) Else, B. G. T.; Papakyriakou, T. N.; Granskog, M. A.; Yackel, J. J. Observations of sea surface fCO₂ distributions and estimated air-sea CO₂ fluxes in the Hudson Bay region (Canada) during the open water season. *J. Geophys. Res.* **2008**, 113, C08026.

(33) Maslanik, J. Stroeve, J. 1999, updated daily. In *Near-Real-Time DMSP SSM/I-SSMIS Daily Polar Gridded Sea Ice Concentrations. 2010–2011*; NASA DAAC at the National Snow and Ice Data Center: Boulder, CO.

(34) Steffen, A.; Bottenheim, J.; Cole, A.; Douglas, T. A.; Ebinghaus, R.; Friess, U.; Netcheva, S.; Nghiem, S.; Sihler, H.; Staebler, R. Atmospheric mercury over sea ice during the OASIS-2009 campaign. *Atmos. Chem. Phys.* **2013**, 13, 7007–7021.

(35) Conaway, C. H.; Black, F. J.; Gault-Ringold, M.; Pennington, J. T.; Chavez, F. P.; Flegal, A. R. Dimethylmercury in coastal upwelling waters, Monterey Bay, California. *Environ. Sci. Technol.* **2009**, 43, 1305–1309.

(36) Mason, R. P.; Sullivan, K. A. The distribution and speciation of mercury in the South and equatorial Atlantic. *Deep Sea Res., Part II* **1999**, 46, 937–956.

(37) Cossa, D.; Martin, J.-M.; Takayanagi, K.; Sanjuan, J. The distribution and cycling of mercury species in the western Mediterranean. *Deep Sea Res., Part II* **1997**, 44, 721–740.

(38) Talmi, Y.; Mesmer, R. Studies on vaporization and halogen decomposition of methyl mercury compounds using GC with a microwave detector. *Water Res.* **1975**, 9, 547–552.

(39) Iverfeldt, Å.; Lindqvist, O. Distribution equilibrium of methyl mercury chloride between water and air. *Atmos. Environ. (1967)* **1982**, 16, 2917–2925.

(40) Niki, H.; Maker, P. D.; Savage, C. M.; Breitenbach, L. P. A long-path Fourier transform infrared study of the kinetics and mechanism for the hydroxyl radical-initiated oxidation of dimethylmercury. *J. Phys. Chem.* **1983**, 87, 4978–4981.

(41) Niki, H.; Maker, P. S.; Savage, C. M.; Breitenbach, L. P. A Fourier-transform infrared study of the kinetics and mechanism of the reaction of atomic chlorine with dimethylmercury. *J. Phys. Chem.* **1983**, 87, 3722–3724.

(42) Slemr, F.; Schuster, G.; Seiler, W. Distribution, speciation, and budget of atmospheric mercury. *J. Phys. Chem.* **1985**, 3, 407–434.

(43) Belzile, C.; Johannessen, S. C.; Gosselin, M.; Demers, S.; Miller, W. L. Ultraviolet attenuation by dissolved and particulate constituents of first-year ice during late spring in an Arctic polynya. *Limnol. Oceanogr.* **2000**, 45, 1265–1273.

(44) Perovich, D. K.; Govoni, J. W. Absorption coefficients of ice from 250 to 400 nm. *Geophys. Res. Lett.* **1991**, 18, 1233–1235.

(45) Ardyna, M.; Gosselin, M.; Michel, C.; Poulin, M.; Tremblay, J.-É. Environmental forcing of phytoplankton community structure and function in the Canadian High Arctic: Contrasting oligotrophic and eutrophic regions. *Mar. Ecol.: Prog. Ser.* **2011**, 442, 37–57.

(46) Heimbürger, L.-E.; Cossa, D.; Marty, J.-C.; Migon, C.; Averty, B.; Dufour, A.; Ras, J. Methyl mercury distributions in relation to the presence of nano- and picophytoplankton in an oceanic water column (Ligurian Sea, North-western Mediterranean). *Geochim. Cosmochim. Acta* **2010**, 74, 5549–5559.

(47) Mason, R.; Rolffhus, K. a.; Fitzgerald, W. Mercury in the north Atlantic. *Mar. Chem.* **1998**, 61, 37–53.

(48) Kirk, J. T. O. *Light and Photosynthesis in Aquatic Ecosystems*; Cambridge University Press, 1994.

(49) Lehnher, I.; St. Louis, V. L.; Emmerton, C. A.; Barker, J. D.; Kirk, J. L. Methylmercury cycling in High Arctic wetland ponds: Sources and sinks. *Environ. Sci. Technol.* **2012**, 46, 10514–10522.

(50) Bloom, N. S.; Watras, C. J. Observations of methylmercury in precipitation. *Sci. Total Environ.* **1989**, 87–88, 199–207.

(51) Graydon, J. A.; Louis, V. L. S.; Hintelmann, H.; Lindberg, S. E.; Sandilands, K. A.; Rudd, J. W. M.; Kelly, C. A.; Hall, B. D.; Mowat, L. D. Long-term wet and dry deposition of total and methyl mercury in the remote boreal ecoregion of Canada. *Environ. Sci. Technol.* **2008**, 42, 8345–8351.

(52) Environment Canada, Historical Climate Data Homepage. <http://climate.weather.gc.ca/> (accessed Nov 3, 2013).

(53) National Snow and Ice Data Center (NSIDC) Arctic Sea Ice News & Analysis. <http://nsidc.org/arcticseaicenews/> (accessed March 4, 2014).