Environmental Science & Technology

ARTICLE

pubs.acs.org/est

Bioavailable Mercury Cycling in Polar Snowpacks

Catherine Larose,[†,‡,§,⊥] Aurélien Dommergue,[*,†] Nicolas Marusczak,[†] Jacques Coves,[∥] Christophe P. Ferrari,[†] and Dominique Schneider[*,‡,§]

[†]Laboratoire de Glaciologie et Géophysique de l'Environnement, CNRS − Université Joseph Fourier Grenoble, 54 Rue Molière, 38400 St Martin d'Hères, France

[‡]Laboratoire Adaptation et Pathogénie des Microorganismes, Université Joseph Fourier Grenoble 1, BP 170, F-38042 Grenoble cedex 9, France

[§]CNRS UMR 5163, France

[∥]Institut de Biologie Structurale, UMR 5075, CNRS CEA UJF, F-38027 Grenoble, France

Supporting Information

ABSTRACT: Polar regions are subject to contamination by mercury (Hg) transported from lower latitudes, severely impacting human and animal health. Atmospheric Mercury Depletion Events (AMDEs) are an episodic process by which Hg is transferred from the atmospheric reservoir to arctic snowpacks. The fate of Hg deposited during these events is the subject of numerous studies, but its speciation remains unclear, especially in terms of environmentally relevant forms such as bioavailable mercury (BioHg). Here, using a bacterial *mer-lux* biosensor, we report the fraction of newly deposited Hg at the surface and at the bottom of the snowpack that is bioavailable. Snow samples were collected over a two-month arctic field campaign in 2008. In surface snow, BioHg is related to atmospheric Hg deposition and snow fall events were shown to contribute to higher proportions of BioHg than AMDEs. Based on our data, AMDEs represent a potential source of 20 $t.y^{-1}$ of BioHg, while wet and dry deposition pathways may provide 135−225 $t.y^{-1}$ of BioHg to Arctic surfaces.

INTRODUCTION

The vulnerability of polar environments to contaminants transported from lower latitudes via long-range atmospheric processes has been the subject of numerous reports.[1,2] The Arctic is sensitive to mercury (Hg),[3] especially coastal sites, which appear to be involved in Hg cycling.[4,5] Hg, a persistent and toxic element, is found both naturally and as an anthropogenically introduced compound in the environment.[6−9] Industrial use of Hg, and its subsequent release to the environment, has contributed to worldwide increases in Hg levels in soil, sediments, and aquatic ecosystems.[10] Although there are no major anthropogenic Hg sources in the Arctic, high levels have been found in the livers and tissues of marine mammals and birds[11,12] leading to increased exposure for Native Communities that depend on these resources.[1]

Transported to the Arctic mainly as gaseous elemental mercury (Hg(0)), Hg can undergo rapid oxidation and deposition during Atmospheric Mercury Depletion Events (AMDEs) in the spring. These events, first discovered at Alert, Canada in 1995,[13] occur via photochemically initiated reactions believed to involve marine halogens[14−16] that oxidize Hg(0) to divalent species. These species can be found in the gas phase or adsorbed to particles and can then be deposited onto snow surfaces at levels 400−800 fold higher than background values over the course of a few hours.[14,17] Although AMDEs have been considered as one of the major Hg sources in arctic regions,[18] field studies suggest that a large fraction of AMDE-derived Hg is re-emitted to the atmosphere following deposition.[17,19,20] However, some Hg remains and can potentially be transferred to deeper layers of the snowpack.[21] This may lead to ecosystem contamination following spring melt, but uncertainties regarding the fate of this Hg and its speciation remain. One field study suggests that some of this newly deposited Hg is bioavailable, i.e. able to cross biological membranes.[16,22] The concept of metal bioavailability is complex, and the fraction of a metal able to penetrate and interact with organisms depends on interdependent chemical, physical, and biological factors such as, for example, ligand concentration, chemical speciation of the metal and pH.[23,24] Bioavailability is an important factor in determining Hg toxicity since several environmental biogeochemical Hg transformations are

Received: September 2, 2010
Accepted: February 2, 2011
Revised: January 31, 2011
Published: February 22, 2011

dx.doi.org/10.1021/es103016x | *Environ. Sci. Technol.* 2011, 45, 2150–2156

enzymatically catalyzed within the cytoplasm of bacterial cells.[25] An example of one such transformation is microbial methylation of divalent mercury to methylmercury (MeHg),[26,27] a highly toxic organo-metallic compound that can bioaccumulate and magnify up through the food chain.[28]

Although determining bioavailable Hg (BioHg) is essential for understanding the fate of deposited Hg, it has rarely been carried out in polar ecosystems, owing to technical limitations. Traditional instruments with high sensitivity and reproducibility are able to measure trace Hg levels in a variety of matrices but are unable to estimate the fraction of Hg that can potentially interact with cells. A number of molecular tools, such as whole cell and protein-based Hg biosensors have been designed,[29−33] but few of these have been used in the field. In the single field study that characterized the bioavailable fraction of Hg in arctic environments, a relatively small proportion of BioHg (13%) was reported in one snow sample collected in May increasing up to 55% in another sample collected at the early stage of melt.[16] However, BioHg was determined in only a limited amount of samples, and no biosensors have been used since in arctic Hg field studies, leading to critical gaps in knowledge.

Here, we present BioHg data from a seasonal Arctic snowpack sampled over a two-month period in the spring of 2008 in Ny-Ålesund (Svalbard, Norway, 79°N). This period included several AMDEs during the third week of April. We detected BioHg in the field using a highly sensitive biosensor designed in our laboratory. In this paper, we further analyzed and expanded on the specific issue of BioHg that was measured as part of a larger research effort on snowpack chemical dynamics[21] and focused on atmospheric sources of BioHg and its cycling within the snowpack. To our knowledge, this data set constitutes the longest series of BioHg measured to date.

MATERIALS AND METHODS

Field Site Description and Sampling. Snowpack mercury concentrations were monitored during a research campaign held between April 16th, 2008 and June 08th, 2008 at Ny-Ålesund, Svalbard, Norway (78°56′N, 11°52′E). The field site is located along the south coast of the Kongsfjorden, which is oriented east−west and open to the sea on the west side and the snowpack is located on land. Surface snow samples (upper 1−3 cm of a ∼0.5 m^2 area) were collected daily. Twice a week, a shallow pit was dug, and both surface and basal samples were collected for Hg analysis. The basal snow layer, made up primarily of several centimeters of depth hoar crystals, was sampled in a homogeneous layer just above the frozen ground. Samples were collected in acid-washed 250 mL glass bottles (Schott) using clean sampling techniques.[34] Snow samples were left to melt at room temperature in the dark, and aliquots were taken for total Hg and BioHg measurements.

Snowpack Characteristics. The snowpack evolved over time. The depth of the snowpack was ∼40 cm at the beginning of the field study and gradually declined throughout the season. A detailed analysis of snowpack physics was not undertaken in the field, but a rough description can be given. Several snow fall events occurred throughout the sampling period, and changes in the crystal morphology of the freshly fallen snow were observed. The snowpack was also vertically stratified, with recognizable crystals at the top, then faceted crystals a couple of centimeters below and depth hoar at the bottom. Depth hoar is formed by snow crystal metamorphism as a result of the redistribution of water vapor due to temperature gradients in the snowpack.[35] This metamorphism leads to rounded crystals with a lower specific surface area (SSA) than freshly fallen snow.[36] At times, very thin melt crusts were observed. By June eighth, most of the snowpack had melted.

Construction of the mer-lux Biosensor. The biosensor's construction was based on that developed by Omura et al.,[33] which was reported to detect bioavailable Hg in the picomolar range. Bacteria *Escherichia coli* JM 109 was transformed with plasmid pNM2, containing the DNA locus from *Cupriavidus metallidurans* CH34 that carries the *merR* and *merT* genes together with their operator/promoter region driving the transcription of the reporter *lux* genes in the pSBluc vector. The *mer-lux* biosensor (*E. Coli* JM109::pNM2) was stored at −80 °C in 20% glycerol until further use. The construct is presented in Figure S1 of the Supporting Information.

The biosensor was tested in the laboratory in order to determine optimal conditions. We tested for cell density, growth phase, specificity, and detection limit. All tests were carried out at 37 °C in LB culture medium supplemented with 100 $\mu g.mL^{-1}$ ampicillin. Bacterial cells were harvested at different time points (early and midexponential phase, stationary phase), diluted, and exposed to different concentrations of Hg (added in a 1:1 (v/v) ratio, with a final volume of 100 μL) in order to verify the linearity of the biosensor's response and its detection limit. After two hours of incubation at 37 °C, luminescence was measured in each sample using a luminometer (Modulus).

Dose−Response and Specificity of the mer-lux Biosensor. We performed two types of control assays to ensure that the biosensor could detect variable BioHg levels in a wide range of samples, representing conditions ranging from AMDEs up until snowmelt.

First, we carried out a series of calibration curves with different known Hg(II) concentrations (NIST SRM-3133 Hg standard). The biosensor responded in a linear manner to Hg(II) in the 0.5 to 50 $ng \cdot L^{-1}$ range (Figure S2 of the Supporting Information). These ranges cover levels for total Hg typically measured in arctic snow in absence of AMDEs. We established a detection limit of 0.5 $ng \cdot L^{-1}$ for our biosensor, calculated as three times the standard deviation of 5 blanks. This was carried out both in the field and in the laboratory. Therefore, the biosensor is sufficiently sensitive for the detection of BioHg in arctic samples. The enhanced sensitivity of our biosensor may be due to the inclusion of *merT* in our construct. The *merT* gene encodes MerT, a Hg(II)-binding membrane protein that allows Hg to efficiently enter the cell[37] and Pepi et al.[38] suggested that the presence of this specific Hg(II) transport system could result in a more sensitive biosensor. However, Selifonova et al.[29] only observed a moderate increase in sensitivity with *merT*. It is possible that our biosensor slightly overestimates the amount of BioHg that can enter the cytoplasm of cells without MerT.

Second, comparative assays with Hg and other metal cations revealed the very high specificity of the biosensor (Figure S3 of the Supporting Information). These assays were carried out at concentrations ranging from 0 to 500 $ng \cdot L^{-1}$ for mercury ($HgCl_2$), zinc (CH_3COOZn), cobalt ($CoCl_2$), lead (CH_3COOPb), copper ($CuCl_2$), nickel ($NiCl_2$), and cadmium ($CdCl_2$). The other heavy metal cations had no significant effect on luminescence induction, suggesting that our *mer-lux* biosensor is highly specific to the targeted Hg(II) ion over this concentration range.

In addition, although our biosensor contains *merT*, which has previously been shown to induce hyper-sensitivity to Hg(II) at

high Hg concentrations,[33,37] luminescence induction at the highest Hg concentration tested (500 ng·L^{-1}) was not affected. Some background luminescence was registered in the absence of added metals, which suggests background expression of *lux* genes that is not metal-related. This has been observed for other biosensors e.g. ref 39 and may be due to promoter leakage, to metal impurities in the test medium, or to the number of copies of the plasmid that were present in the cells.[39] The biosensor responded in a dose-dependent manner to Hg stress even in suboptimal growth conditions (the field site lacked agitators for the incubator) and was convenient to handle in the field without the need for substrate addition.

Field Measurements. Total Hg (THg) concentrations were measured in triplicate with a Tekran model 2600 using USEPA method 1631 revision E. BioHg was detected using the *mer-lux* biosensor that was cultured overnight in LB medium containing 100 μg.mL^{-1} ampicillin at 37 °C without agitation. The culture was resuspended in LB medium, and experiments were carried out using cells in midexponential growth phase (OD600 = 0.4). Cells were exposed to either a series of Hg dilutions (0.5 to 50 ng·L^{-1} in sterilized, mercury-free saline solution) in order to obtain a standard curve or to melted snow samples with unknown bioavailable Hg concentrations in a 1:1 v/v ratio and incubated for two hours at 37 °C without agitation. The Hg standards were prepared from serial dilutions of a monoelemental Hg(II) solution (NIST SRM-3133 Hg standard) and applied to the biosensor with the same proportion as the samples. The solution used for preparing the standard curve was calibrated such that it contained comparable amounts of ions as found in those of our snow samples (based on previous field data, for ion concentrations, please consult the SI). Samples were analyzed in triplicate (using three independent cultures), and light emission was recorded using a luminometer (Modulus). Luminescence was expressed as relative light units (RLU) and normalized for optical density (measured with a spectrophotometer) as well as for background luminescence. Analytical reproducibility varied between 5% and 15%.

Statistics. All data were log-transformed prior to regression analysis in order to obtain data with a normal distribution. The transformation was successful for all data. Statistical data analysis was performed using JMP 9.0 software (SAS Institute, 2003). Simple linear regression analysis was carried out to detect associations between BioHg and THg and slopes were compared in surface and basal samples using analysis of covariance (ANCOVA). Regression analysis for all chemical data are reported elsewhere, but no significant correlations with major ion chemistry were observed.[21] Analysis of variance (ANOVA) and Tukey-Kramer HSD multiple comparison tests were carried out to compare BioHg to THg ratios among different sample types. Statistical significance was set at a probability level $\alpha < 0.05$.

RESULTS AND DISCUSSION

Considerations on BioHg Measurements. Bioavailability of Hg depends on a variety of factors including pH and the Hg-complexing ligand concentrations that are found both within the sample and the assay media. Since our biosensor measurements were conducted in LB growth medium and the snow was melted prior to analysis, the BioHg values obtained do not reflect the *in situ* chemistry of the snow. The values, however, do present an estimate of the fraction of Hg(II) that is labile in a snowpack. Therefore, given the complexity in determining the exact chemical form of BioHg in environmental samples, we define BioHg as the amount of Hg(II) able to cross biological membranes and interact with the sensing element of our biosensor.

Springtime BioHg and THg in Snowpacks. Between the 16th of April and the 07th of June 2008, we measured THg and BioHg concentrations in surface and basal snow samples. Data are presented in Figure 1. A detailed discussion on snowpack chemistry and THg behavior can be found elsewhere.[21] Several AMDEs occurred during spring at the field site. These first events were observed in March (before sampling began), and others were recorded between the 17th and 25th of April.[40] The April events were associated with high particulate Hg (PHg) and low reactive gaseous mercury (RGM) concentrations.[41] The AMDE period revealed high levels of both THg (up to 148.9 ng·L^{-1}) and BioHg (up to 16.2 ng·L^{-1}) deposition on surface snow. These levels decreased as the season progressed. One measurement from May showed a comparable value of BioHg of 8.8 ng·L^{-1} in surface snow at Barrow (Alaska).[16] We simulated the potential inorganic speciation of mercury using a commercial chemical equilibrium program (Visual MINTEQ v2.61), with parameters such as chemical equilibrium, major ions, pH, and some short chain organic compounds. In the calculation, the potential speciation of Hg is driven by high chloride and, to a lesser extent, bromide concentrations and an acidic pH. However, this model does not take into account organic molecules that alter Hg speciation and bioavailability in the snow and therefore does not accurately reflect *in situ* speciation. Based on these simulations, most of our snow samples contained a large proportion of $HgCl_2$ complexes, followed by HgBrCl, $HgCl_3^-$, and $HgBr_2$, although a competition between chloride and other ligands is likely. We have also carried out the simulation on the BioHg assay medium (melted snow sample plus growth medium). The model predicted that the potential speciation of Hg was mainly chlorocomplexes; however, this simulation does not include organic molecules. Based on previous laboratory studies, these neutrally charged species are bioavailable and able to cross biological membranes by passive diffusion;[30,42] therefore, we expected that our samples would contain a large fraction of BioHg. However, BioHg concentrations varied throughout the season in both surface and basal samples and only rarely represented 100% of the THg fraction. High chloride concentrations and large fractions of particle-bound mercury may have limited bacterial uptake.[30,42,43] A significant positive correlation ($p < 0.0001$) was observed between THg and BioHg levels measured across all of our snow samples (Figure 2). This would suggest that BioHg is dependent on atmospheric Hg deposition processes. During AMDEs, BioHg concentrations are among the highest observed (Figure 1b). However, a portion is probably photoreducible and hence likely evaded back to the atmosphere, which would account for the concomitant drop in both THg and BioHg concentrations following the AMDEs, consistent with the high Hg(0) evasion fluxes measured during the same period.[40]

Hg concentrations were less variable in basal samples. At the beginning of the field study, the bottom of the snowpack showed low but similar THg and BioHg levels (~2 ng·L^{-1}). Given that several AMDEs and snow fall events occurred in March before sampling began,[41] these values do not necessarily represent baseline, or pre-AMDE snow Hg levels. THg levels stayed roughly constant with the exception of two increases, one on May sixth and one on May 20th. The first increase was observed just after AMDEs and it is likely that THg was transferred into deeper layers of the snowpack from the surface.[21,44,45] The second

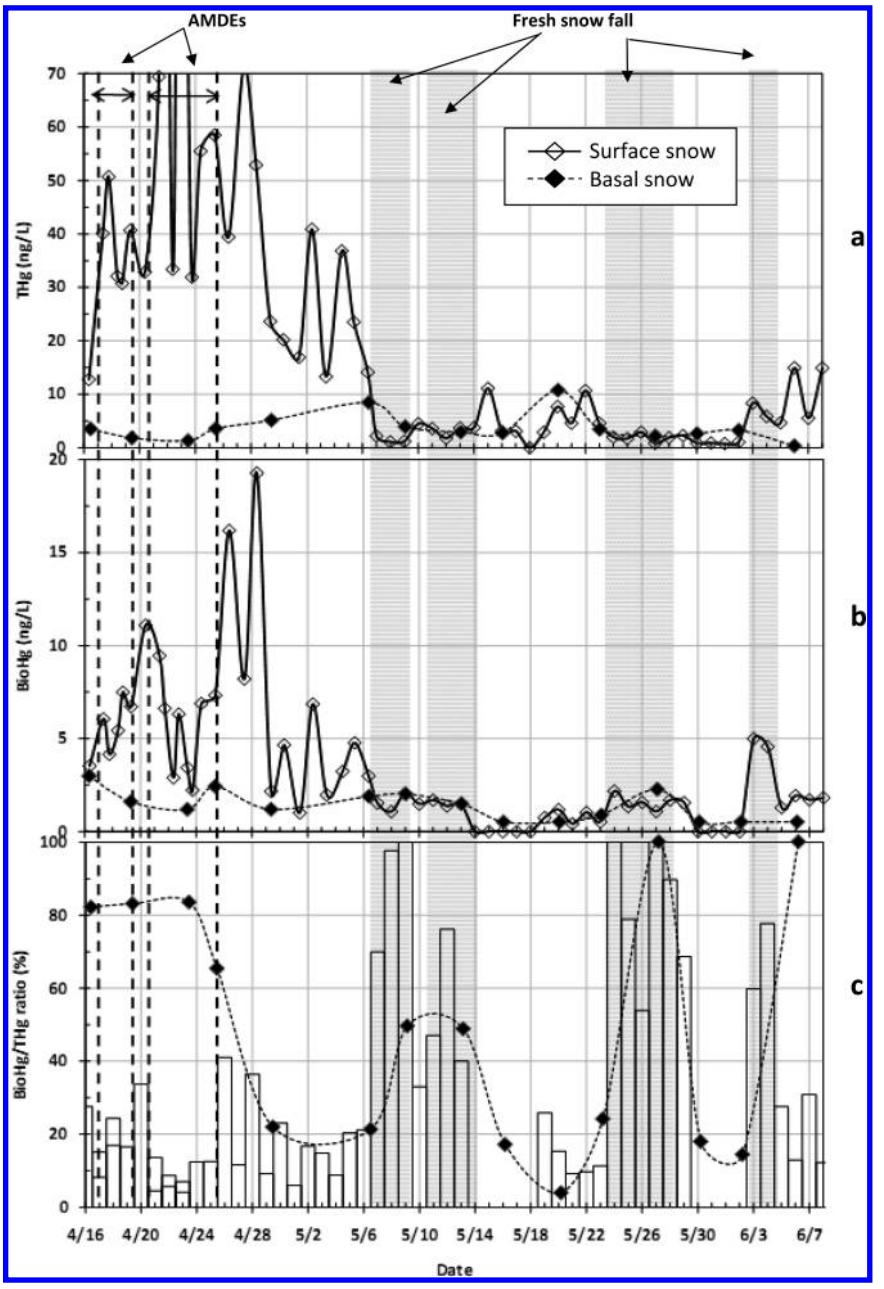

Figure 1. Concentrations of mercury species in surface and basal snow samples of an arctic snowpack. (**a**) THg concentrations measured in surface and basal snow samples. Error bars for THg were typically less than 0.2 ng·L^{-1} and therefore could not be represented here. Two THg concentration peaks (148.9 ng·L^{-1} and 110.6 ng·L^{-1} on April 21th and April 22th, respectively) were omitted from this graph for clarity. (**b**) BioHg concentrations measured in surface and basal snow samples. BioHg was not measured in surface samples (0 ng·L^{-1}) for the periods May 14 to 18 and May 30 to June 2. (**c**) Ratios of BioHg over THg calculated in surface and basal snow samples. Ratios in surface snow were not available for the periods May 14 to 18 and May 30 to June 2 due to the absence of BioHg data.

increase in basal snow THg levels may be connected to spring snowmelt.[21]

AMDEs as a BioHg Source. In order to determine the relative importance of AMDEs as a BioHg source to snowpacks, we compared the BioHg/THg ratio in samples during different events (AMDEs, wet deposition) (Figure 1c). Snow sample type (fresh, AMDE, and other) explained 80% of the variance in BioHg/THg ratios ($p < 0.0001$) and fresh snow had significantly higher ratios than both other types of snow (Tukey-Kramer HSD multiple comparison test, Figure S4). The ratio varied throughout the field study, with values between ~5 and 100% in both surface and basal snow. BioHg/THg ratios in basal snow mirror changes in surface snow ratios with the exception of the AMDE period. This would suggest that the snowpack is permeable, that some of the deposited Hg is mobile, and that both THg and BioHg are transferred to the base of the snowpack. Based on the BioHg/THg ratios in basal samples as compared to surface sample values over the whole sampling period, different transfer efficiencies appear to exist. The lower ratios in the deeper layers of the snowpack (sampled on the 10th and 14th of May) may reflect reduced Hg adsorption to snow. This may be linked to snow crystal morphology since the basal layer consisted mainly of

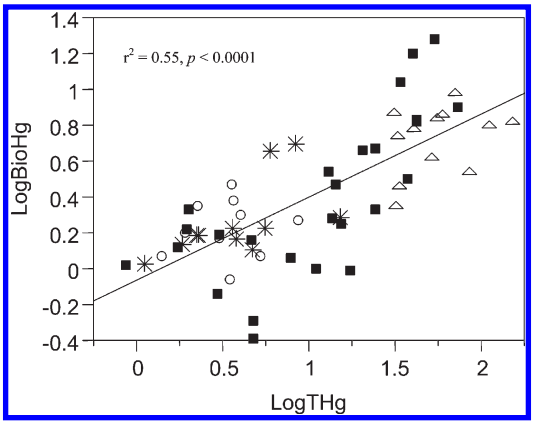

Figure 2. Linear relationship between THg and BioHg with log-transformed data in snow samples. Significance levels were determined using the F-test ($p < 0.0001$). Open circles represent basal samples, open triangles represent AMDE samples, stars represent fresh snow samples, and closed squares represent unclassified surface snow samples.

depth hoar, which has a low specific surface area (SSA). The higher ratios (~100%) observed in the late May (27th) sample are likely linked to enrichment in surface meltwater at base of the snow, since the snowpack went isothermal on the 20th of May. Melting mobilizes soluble chemicals;[46] therefore, labile species were likely transferred to the base of the snowpack.

In surface samples collected during AMDEs, the relative amount of BioHg represented less than 20% of THg, despite the high Hg levels deposited (Figure 1c, dotted lines). This is in agreement with the snow sample collected in May at Barrow (Alaska) that showed a BioHg fraction of 13%.[16] Both of these events were characterized by high atmospheric particulate Hg concentrations (370 $pg.m^{-3}$).[41] Therefore, the majority of Hg deposited during these AMDEs was likely particle-bound and, in turn, less bioavailable. It is likely that the speciation of oxidized Hg in the atmosphere (particulate vs gaseous) will have a direct impact on the levels of surface snow BioHg concentrations. Higher percentages between the two AMDEs (16th and 20th of April) were associated with the occurrence of non Hg(0)-depleted air masses.[40] However, during the AMDEs at the beginning of the field season, the BioHg/THg ratio in basal snow was exceptionally high with values close to 80%. The reasons for these high values are unclear.

In contrast, fresh snow events were always associated with an increase in the percent of BioHg relative to THg in surface samples. A constant source of reactive and bioavailable Hg was therefore scavenged from the atmosphere, and its relative proportion strongly increased during wet deposition. Increases in BioHg/THg ratios are also seen at the base of the snowpack, supporting the hypothesis of efficient Hg transfer. The ratios increased to 100% in both surface and basal samples on May 27th, a period associated with both snowfall and active melt in the snowpack.

It would appear that in terms of relative concentrations, precipitation events are a larger source of BioHg to snowpacks than AMDEs, but further studies of BioHg and THg fractions in precipitation should be carried out. If this hypothesis is verified, then precipitation events will have important consequences on mercury cycling in the Arctic, given that they occur throughout the entire year. AMDEs should not be discounted as sources of BioHg to ecosystems, because high concentrations are deposited, but these events occur less frequently on an annual scale than wet deposition events. Modeling estimates[18] have suggested that AMDEs deposit 100 $t.y^{-1}$ of Hg to the Arctic (north of 60°N), while wet and dry deposition represents 225 $t.y^{-1}$. Based on our data set, AMDEs may represent a potential BioHg source of only 20 t y^{-1} (calculated with a BioHg/THg ratio of 20%) to the Arctic. This contribution is minimal when compared to wet and dry deposition pathways, which can potentially provide 135−225 t y^{-1} of BioHg (ratio 60−100%) to surface snow.[18] BioHg can then be transferred to other ecosystems by meltwater as observed by the BioHg/THg ratio in meltwaters that are comprised between 20 and 50% (data not shown). These estimates need to be considered carefully, given that they were calculated from modeling results of wet and dry deposition, since no experimental data for arctic sites is available. The results presented here may impact Hg mass-balance models for Polar Regions, especially in the context of the effects of climate change on contaminant cycling, since predictions for the Arctic include increases in precipitation.[1] Based on our results, this would lead to an increase in BioHg to arctic snowpacks, but this assessment has to be considered carefully because we are basing our estimates on a relatively short field study that is specific to a coastal arctic site.

■ ASSOCIATED CONTENT

Supporting Information. Figure S1 showing construction of *mer-lux* fusion plasmid pNM2 for the detection of BioHg. Figure S2 showing *mer-lux* biosensor calibration curve. Figure S3 showing *mer-lux* biosensor response in relative light units to mercury and other metals. Figure S4 showing analysis of variance for BioHg/THg ratios as a function of snow type in surface snow samples. Table S1 showing summary for pH, THg, BioHg, and major ions. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: dommergue@lgge.obs.ujf-grenoble.fr (A.D.); dominique.schneider@ujf-grenoble.fr (D.S.).

Present Addresses

⊥Environmental Microbial Genomics Group, Laboratoire AMPERE, UMR CNRS 5005, Ecole Centrale de Lyon, France.

■ ACKNOWLEDGMENT

This work was funded by INSU/CNRS (EC2CO and LEFE-CHAT 32), Université Joseph Fourier − Grenoble (pôle TUNES 2007), and CNRS. Logistical support was provided by the French Polar Institute IPEV (program CHIMERPOL 399). We acknowledge Alan Le Tressoler, Nicolas Soumis, and AWI-PEV for field support. We thank Ralf Ebinghaus and GKSS for analytical support. We would also like to thank A. J. Poulain, T. Barkay, D. A. Durnford, and A. P. Dastoor for their helpful comments on the manuscript. C.L. would like to acknowledge the FQRNT (Le Fonds Québécois de la Recherche sur la Nature et les Technologies) for a Ph.D. research fellowship. C.F. thanks the Institut Universitaire de France (IUF) for its financial support.

■ REFERENCES

(1) AMAP. *AMAP Assessment 2009: Human Health in the Arctic. Arctic Monitoring and Assessment Programme (AMAP)*; Oslo, Norway, 2009; p 256.

(2) Macdonald, R. W. Climate change, risks and contaminants: A perspective from studying the Arctic. *Hum. Ecol. Risk Assess.* **2005**, *11* (6), 1099–1104.

(3) Barkay, T.; Poulain, A. J. Mercury (micro)biogeochemistry in polar environments. *FEMS Microbiol. Ecol.* **2007**, *59* (2), 232–241.

(4) Steffen, A.; Douglas, T.; Amyot, M.; Ariya, P.; Aspmo, K.; Berg, T.; Bottenheim, J.; Brooks, S.; Cobbett, F.; Dastoor, A.; Dommergue, A.; Ebinghaus, R.; Ferrari, C.; Gardfeldt, K.; Goodsite, M. E.; Lean, D.; Poulain, A. J.; Scherz, C.; Skov, H.; Sommar, J.; Temme, C. A synthesis of atmospheric mercury depletion event chemistry in the atmosphere and snow. *Atmos. Chem. Phys.* **2008**, *8* (6), 1445–1482.

(5) Poulain, A. J.; Ni Chadhain, S. M.; Ariya, P. A.; Amyot, M.; Garcia, E.; Campbell, P. G. C.; Zylstra, G. J.; Barkay, T. Potential for mercury reduction by microbes in the high arctic. *Appl. Environ. Microbiol.* **2007**, *73* (7), 2230–2238.

(6) Nriagu, J. O.; Pacyna, J. M. Quantitative Assessment of Worldwide Contamination of Air, Water and Soils by Trace-Metals. *Nature* **1988**, *333* (6169), 134–139.

(7) Nriagu, J. O. A global assessment of natural sources of atmospheric trace metals. *Nature* **1989**, *338*, 47–49.

(8) Fitzgerald, W. F.; Engstrom, D. R.; Mason, R. P.; Nater, E. A. The case for atmospheric mercury contamination in remote areas. *Environ. Sci. Technol.* **1998**, *32* (1), 1–7.

(9) Lindberg, S.; Bullock, R.; Ebinghaus, R.; Engstrom, D.; Feng, X. B.; 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* (1), 19–32.

(10) Gray, J. E.; Hines, M. E. Mercury: Distribution, transport, and geochemical and microbial transformations from natural and anthropogenic sources - Preface. *Appl. Geochem.* **2006**, *21* (11), 1819–1820.

(11) Campbell, L. M.; Norstrom, R. J.; Hobson, K. A.; Muir, D. C. G.; 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.

(12) Braune, B. M.; Outridge, P. M.; Fisk, A. T.; Muir, D. C. G.; Helm, P. A.; Hobbs, K.; Hoekstra, P. F.; Kuzyk, Z. A.; Kwan, M.; Letcher, R. J.; Lockhart, W. L.; Norstrom, R. J.; Stern, G. A.; Stirling, I. Persistent organic pollutants and mercury in marine biota of the Canadian Arctic: An overview of spatial and temporal trends. *Sci. Total Environ.* **2005**, *351*, 4–56.

(13) Schroeder, W. H.; Anlauf, K. G.; Barrie, L. A.; Lu, J. Y.; Steffen, A.; Schneeberger, D. R.; Berg, T. Arctic springtime depletion of mercury. *Nature* **1998**, *394* (6691), 331–332.

(14) Lu, J. Y.; Schroeder, W. H.; Barrie, L. A.; Steffen, A.; Welch, H. E.; Martin, K.; Lockhart, L.; Hunt, R. V.; Boila, G.; Richter, A. Magnification of atmospheric mercury deposition to polar regions in springtime: the link to tropospheric ozone depletion chemistry. *Geophys. Res. Lett.* **2001**, *28* (17), 3219–3222.

(15) Skov, H.; Christensen, J. H.; Goodsite, M. E.; Heidam, N. Z.; Jensen, B.; Wahlin, P.; Geernaert, G. Fate of elemental mercury in the arctic during atmospheric mercury depletion episodes and the load of atmospheric mercury to the arctic. *Environ. Sci. Technol.* **2004**, *38* (8), 2373–2382.

(16) Lindberg, S. E.; Brooks, S.; Lin, C. J.; Scott, K. J.; Landis, M. S.; Stevens, R. K.; Goodsite, M.; Richter, A. Dynamic Oxidation of Gaseous Mercury in the Arctic Troposphere at Polar Sunrise. *Environ. Sci. Technol.* **2002**, *36* (6), 1245–256.

(17) Dommergue, A.; Larose, C.; Faïn, X.; Clarisse, O.; Foucher, D.; Hintelmann, H.; Schneider, D.; Ferrari, C. P. Deposition of mercury species in the Ny-Ålesund area (79°N) and their transfer during snowmelt. *Environ. Sci. Technol.* **2010**, *44* (3), 901–907.

(18) Ariya, P. A.; Dastoor, A. P.; Amyot, M.; Schroeder, W. H.; Barrie, L.; Anlauf, K.; Raofie, F.; Ryzhkov, A.; Davignon, D.; Lalonde, J.; Steffen, A. The Arctic: a sink for mercury. *Tellus B* **2004**, *56* (5), 397–403.

(19) Poulain, A. J.; Lalonde, J. D.; Amyot, M.; Shead, J. A.; Raofie, F.; Ariya, P. A. Redox transformations of mercury in an Arctic snowpack at springtime. *Atmos. Environ.* **2004**, *38* (39), 6763–6774.

(20) Kirk, J. L.; St. Louis, V. L.; Sharp, M. J. Rapid reduction and reemission of mercury deposited into snow packs during atmospheric mercury depletion events at Churchill, Manitoba, Canada. *Environ. Sci. Technol.* **2006**, *40*, 7590–7596.

(21) Larose, C.; Dommergue, A.; De Angelis, M.; Cossa, D.; Averty, B.; Marusczak, N.; Soumis, N.; Schneider, D.; Ferrari, C. Springtime changes in snow chemistry lead to new insights into mercury methylation in the Arctic. *Geochim. Cosmochim. Acta* **2010**, *74*, 6263–6275.

(22) Scott, K. J. Bioavailable mercury in arctic snow determined by a light-emitting mer-lux bioreporter. *Arctic* **2001**, *54* (1), 92–95.

(23) Barrocas, P. R. G.; Landing, W. M.; Hudson, R. J. M. Assessment of mercury(II) bioavailability using a bioluminescent bacterial biosensor: Practical and theoretical challenges. *J. Environ. Sci.* **2010**, *22* (8), 1137–1143.

(24) Barkay, T.; Turner, R. R.; Rasmussen, L. D.; Kelly, C. A.; Rudd, J. W., Luminescence-facilitated detection of bioavailable mercury in natural waters. In *Bioluminescence Methods and Protocols 102*; Robert, A., LaRossa, Eds.; Humana Press Inc.: NJ, 1998; pp 231−246.

(25) Golding, G. R.; Kelly, C. A.; Sparling, R.; Loewen, P. C.; Barkay, T. Evaluation of mercury toxicity as a predictor of mercury bioavailability. *Environ. Sci. Technol.* **2007**, *41* (16), 5685–5692.

(26) Compeau, G. C.; Bartha, R. Sulfate-Reducing Bacteria - Principal Methylators of Mercury in Anoxic Estuarine Sediment. *Appl. Environ. Microbiol.* **1985**, *50* (2), 498–502.

(27) Fleming, E. J.; Mack, E. E.; Green, P. G.; Nelson, D. C. Mercury methylation from unexpected sources: Molybdate-inhibited freshwater sediments and an iron-reducing bacterium. *Appl. Environ. Microbiol.* **2006**, *72* (1), 457–464.

(28) Boudou, A.; Ribeyre, F. Experimental-Study of Trophic Contamination of Salmo-Gairdneri by 2 Mercury-Compounds - $HgCl_2$ and CH_3HgCl - Analysis at the Organism and Organ Levels. *Water, Air, Soil Pollut.* **1985**, *26* (2), 137–148.

(29) Selifonova, O.; Burlage, R.; Barkay, T. Bioluminescent Sensors for Detection of Bioavailable Hg(II) in the Environment. *Appl. Environ. Microbiol.* **1993**, *59* (9), 3083–3090.

(30) Barkay, T.; Gillman, M.; Turner, R. R. Effects of dissolved organic carbon and salinity on bioavailability of mercury. *Appl. Environ. Microbiol.* **1997**, *63* (11), 4267–4271.

(31) Ivask, A.; Virta, M.; Kahru, A. Construction and use of specific luminescent recombinant bacterial sensors for the assessment of bioavailable fraction of cadmium, zinc, mercury and chromium in the soil. *Soil Biol. Biochem.* **2002**, *34* (10), 1439–1447.

(32) Hansen, L. H.; Sorensen, S. J. Versatile biosensor vectors for detection and quantification of mercury. *FEMS Microbiol. Lett.* **2000**, *193* (1), 123–127.

(33) Omura, T.; Kiyono, M.; Pan-Hou, H. Development of a specific and sensitive bacteria sensor for detection of mercury at picomolar levels in environment. *J. Health Sci.* **2004**, *50* (4), 379–383.

(34) Ferrari, C. P.; Moreau, A. L.; Boutron, C. F. Clean conditions for the determination of ultra−low levels of mercury in ice and snow samples. *Fresenius' J. Anal. Chem.* **2000**, *366*, 433–437.

(35) Sturm, M.; Benson, C. S. Vapor transport, grain growth and depth-hoar development in the subarctic snow. *J. Glaciol.* **1997**, *43* (143), 42–59.

(36) Taillandier, A. S.; Domine, F.; Simpson, W. R.; Sturm, M.; Douglas, T. A.; Severin, K. Evolution of the Snow Area Index of the Subarctic Snowpack in Central Alaska over a Whole Season. Consequences for the Air to Snow Transfer of Pollutants. *Environ. Sci. Technol.* **2006**, *40* (24), 7521–7527.

(37) Hamlett, N. V.; Landale, E. C.; Davis, B. H.; Summers, A. O. Roles of the Tn21 merT, merP, and merC gene products in mercury resistance and mercury binding. *J. Bacteriol.* **1992**, *174*, 6377–6385.

(38) Pepi, M.; Reniero, D.; Baldi, F.; Barbieri, P. A comparison of MER:: LUX whole cell biosensors and moss, a bioindicator, for estimating mercury pollution. *Water, Air, Soil Pollut.* **2006**, *173* (1−4), 163–175.

(39) Ivask, A.; Rolova, T.; Kahru, A. A suite of recombinant luminescent bacterial strains for the quantification of bioavailable heavy metals and toxicity testing. *BMC Biotechnol.* **2009**, *9*.

(40) Steen, A. O.; Berg, T.; Dastoor, A. P.; Durnford, D. A.; Hole, L. R.; Pfaffhuber, K. A. Dynamic exchange of gaseous elemental mercury during polar night and day. *Atmos. Environ.* **2009**, *43* (35), 5604–5610.

(41) Steen, A. O.; Berg, T.; Dastoor, A. P.; Durnford, D. A.; Hole, L. R.; Pfaffhuber, K. A. Natural and anthropogenic atmospheric mercury in the European Arctic: a speciation study. *Atmos. Chem. Phys. Discuss.* **2010**, *10* (11), 27255–27281.

(42) Gutknecht, J. Inorganic Mercury (Hg^{2+}) Transport through Lipid Bilayer-Membranes. *J. Membr. Biol.* **1981**, *61* (1), 61–66.

(43) Compeau, G. C.; Bartha, R. Effect of Salinity on Mercury-Methylating Activity of Sulfate-Reducing Bacteria in Estuarine Sediments. *Appl. Environ. Microbiol.* **1987**, *53* (2), 261–265.

(44) Daly, G. L.; Wania, F. Simulating the influence of snow on the fate of organic compounds. *Environ. Sci. Technol.* **2004**, *38* (15), 4176–4186.

(45) Johnson, K. P.; Blum, J. D.; Keeler, G. J.; Douglas, T. A. Investigation of the deposition and emission of mercury in arctic snow during an atmospheric mercury depletion event. *J. Geophys. Res., [Atmos.]* **2008**, *113* (D17).

(46) Tranter, M.; Brimblecombe, P.; Davies, T. D.; Vincent, C. E.; Abrahams, P. W.; Blackwood, I. The composition of snowfall, snowpack and meltwater in the Scottish Highlands - Evidence for preferential elution. *Atmos. Environ.* **1986**, *20* (3), 517–525.