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June 2021

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Final report

Approved for public release; distribution is unlimited.

Prepared for National Science Foundation, Office of Polar Programs
Alexandria, Virginia 22314

Under Grant Numbers ARC-0435989 and ARC-0435893

Preface

This study was conducted for the U.S. National Science Foundation, Office of Polar Programs, under Grant Number ARC-0435989 and University of Michigan, Grant Number ARC-0435893.

The work was performed by the Biogeochemical Sciences Branch of the Research and Engineering Division, U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory (ERDC-CRREL). At the time of publication, Dr. Justin B. Berman was Branch Chief, and Dr. George Calfas was Division Chief. The Deputy Director of ERDC-CRREL was Mr. David B. Ringelberg, and the Director was Dr. Joseph L. Corriveau.

Extensive logistical support was provided by the Barrow Arctic Science Consortium, and their assistance is greatly appreciated. Numerous colleagues assisted with sample collection and hearty discussions of the Arctic mercury cycle, particularly M. Sturm, C. Polashenski, A. Steffen, and L. Sherman. We thank anonymous reviewers for their comments on earlier versions of the manuscript.

This paper was originally published by the American Chemical Society in the *Environmental Science and Technology Letters* on 7 March 2019.

The Commander of ERDC was COL Teresa A. Schlosser and the Director was Dr. David W. Pittman.

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ABSTRACT: Springtime atmospheric mercury depletion events (AMDEs) lead to snow with elevated mercury concentrations (>200 ng Hg/L) in the Arctic and Antarctic. During AMDEs gaseous elemental mercury (GEM) is photochemically oxidized by halogens to reactive gaseous mercury which is deposited to the snowpack. This reactive mercury is either photochemically reduced back to GEM and re-emitted to the atmosphere or remains in the snowpack until spring snowmelt. GEM is also deposited to the snowpack and tundra vegetation by reactive surface uptake (dry deposition) from the atmosphere. There is little consensus on the proportion of AMDE-sourced Hg versus Hg from dry deposition that is released in spring runoff. We used mercury stable isotope measurements of GEM, snowfall, snowpack, snowmelt, surface water, vegetation, and peat from a northern Alaska coastal watershed to quantify Hg sources. Although high Hg concentrations are deposited to the snowpack during AMDEs, we estimate that ~76 to 91% is released back to the atmosphere prior to snowmelt. Mercury deposited to the snowpack as GEM comprises the majority of snowmelt Hg and has a Hg stable isotope composition similar to Hg deposited by reactive surface uptake of GEM into the leaves of trees in temperate forests. This GEM-sourced Hg is the dominant Hg we measured in the spring snowpack and in tundra peat permafrost deposits.



1. INTRODUCTION

Elevated mercury (Hg) concentrations have been reported in Arctic coastal snow and ice far from emission sources.^{1,2} This is of concern because Hg can be transformed into its more toxic form, methylmercury, in Arctic wetlands which can be readily biomagnified in aquatic and terrestrial food webs.³⁻⁵ Elevated Hg levels have been reported in fish and piscivorous mammals, both of which are major staples in Arctic subsistence diets.⁶ Since the Arctic is snow and ice covered for up to nine months a year, a majority of the surface water runoff occurs during spring melt.⁷ A major wintertime source of Hg deposition has been attributed to atmospheric mercury depletion events (AMDEs), which are driven by photochemical reactions mediated by reactive halogen compounds in snow and ice.^{8,9} During AMDEs, gaseous elemental Hg, Hg(0), is oxidized to reactive gaseous mercury, Hg(II), which is readily deposited to snow and ice surfaces.¹⁰⁻¹² In addition to the AMDE process, Hg is deposited to the Arctic by reactive deposition of Hg(0) directly from the atmosphere to the snowpack and tundra vegetation.¹³ This Hg(0) can be oxidized and retained in the snowpack, vegetation, and soils; however, the mechanism by which Hg(0) enters the snowpack and is oxidized is not well-known. The snowpack halogen content in Arctic coastal regions is elevated,¹⁴ and this, along with the catalytic properties of snow and ice crystal surfaces,¹⁵ implicates halogens in the Hg oxidation process.¹⁶ Sea ice, particularly

in refreezing open leads, is the dominant source of reactive halogens to the coastal environment.^{14,17-19}

Hg(II) produced in the atmosphere from AMDEs and Hg(II) produced in the snowpack from reactive surface uptake of Hg(0) (hereafter referred to as “dry deposition”) can be photochemically reduced to Hg(0) and emitted back to the atmosphere, or it can remain in the snowpack to become a component of spring melt runoff.^{20,21} Estimates of the percent of AMDE-sourced Hg remaining in the snowpack a week after active AMDE deposition range from 5 to 60% with higher retention reported predominantly from coastal locations.^{22,23} Hg(II) deposited during AMDEs is generally associated with snowfall and dry deposition of small (mm in diameter) ice crystals (diamond dust²). However, Hg(0) can infiltrate into snowpack pore spaces and become oxidized to Hg(II) within the snowpack throughout the winter. Thus, exposure to sunlight, which is needed for photochemical reduction reactions, is expected to be greater for AMDE Hg(II), which is deposited at the snow surface compared to Hg(0), which is deposited within the snowpack by oxidation to Hg(II). It has also been postulated that Hg(II) in halogen-rich snow is less

likely to undergo photoreduction than in halogen-poor snow.^{10,24} Because inland snowpacks have markedly lower halogen ion concentrations compared to coastal sites,²⁵ we would expect a decrease in total Hg deposition and an increase in the percent loss of Hg from the snowpack through re-emission with increasing distance inland. Coastal sites are also more likely than inland ones to have identifiable amounts of AMDE-deposited Hg and higher snowpack Hg concentrations.

The contribution of total yearly Hg deposition attributable to AMDEs in the Arctic versus deposition of Hg(0) from dry deposition has not been well-quantified. However, a recent long-term Hg-deposition mass balance study that focused on Hg sources and sinks at an Arctic Alaskan tundra site ~200 km inland from the coast (Toolik Lake) concluded that little (~5%) of the Hg in the tundra was attributable to Hg(II) from wet deposition including AMDEs, while the majority (73–90%) of the Hg present in the tundra was deposited from atmospheric Hg(0).¹³

In another recent study at a coastal site near Utqiagvik Alaska (formerly known as Barrow) an ionic pulse of elevated major ions and Hg was identified in a small (2.5 ha) watershed during spring snowmelt runoff periods for two subsequent years.²¹ Total dissolved Hg meltwater runoff ranged between 8 and 14 ng/ha in the two years studied. This is up to 7 times greater than runoff reported from noncoastal Arctic locations^{26,27} and markedly greater than runoff from temperate watersheds.²⁸ It was calculated that 41% and 78% of the premelt snowpack total Hg exited the watershed in stream discharge during each of the two spring snowmelt periods, respectively. From these results and time-series measurements of Hg in the snowpack and in meltwater throughout the runoff period it was estimated that ~25% of the Hg in spring melt runoff at the coastal study location was attributable to AMDE Hg.²¹

Numerous studies have established the use of Hg stable isotopes to identify Hg sources and track both photochemical and dark reactions in the environment.²⁹ It has been well-established that photochemical reactions impart large magnitude mass independent fractionation (MIF) and mass dependent fractionation (MDF), whereas non-photochemical reactions impart almost entirely MDF.^{29,30} Snow deposited during AMDEs has Hg isotope ratios with MDF similar to atmospheric GEM but with lower MIF than GEM, indicative of photochemical oxidation of atmospheric Hg(0) followed by deposition of Hg(II) with snowfall.^{12,31}

A study of particular relevance to this study³¹ identified that photochemical reduction of Hg(II) to Hg(0) in the Arctic snowpack after deposition produced MIF with decreasing $\Delta^{199}\text{Hg}$ and $\Delta^{201}\text{Hg}$ in residual snowpack Hg(II). Another study of relevance to this work³² showed that the oxidation of atmospheric Hg(0) within the leaves of plants results in no MIF but imparts an MDF with a shift of ca. -2.0‰ in $\delta^{202}\text{Hg}$ between Hg(0) in the atmosphere and Hg(II) deposited in leaves. A study of boreal forest runoff identified foliar uptake by vegetation, not wet precipitation, as the dominant Hg source.³³ The results of these and other studies were used to help interpret Hg isotope measurements in a previous study of atmosphere, rain, snow, and soils from Toolik Lake Alaska, ~200 km inland from the Arctic Coast.¹³ From this it was concluded that the majority of the Hg flux to the inland tundra (~70%) was via Hg(0) deposition to vegetation and soil. This paper¹³ further argued that neither rain nor AMDE snow contributed significantly to the air–surface Hg flux. This study

was particularly important, because it was the first to conclusively demonstrate that elevated Hg levels in Arctic soils are driven by reactive surface uptake of Hg(0) rather than Hg(II) deposition.

The Toolik Lake study¹³ motivated us to synthesize Hg isotope measurements that we made on samples from Utqiagvik, Alaska, as a comparison location from the Arctic coast in contrast to the previous study¹³ performed ~200 km inland. Our study design utilized sampling the outflow of a closed catchment and allowed us to quantify the mass balance of Hg released by melting of the snowpack.²¹ Numerous studies have shown higher Hg concentrations in coastal compared to inland snowpacks in the Arctic.^{10,26,27,34,35} This is also the case when comparing Toolik Lake snow (0.4–12.5 ng/L)¹³ to Utqiagvik snow (4.1 to >1000 ng/L).^{11,36}

2. MATERIALS AND METHODS

2.1. Study Site. To track the processes by which Hg is deposited from the atmosphere to the Arctic Coastal land surface we measured Hg stable isotopes from a variety of environmental compartments during a spring melt runoff mass balance study in 2008.²¹ Our sampling was focused at the snowNET site on the Arctic Coastal Plain of Alaska 6 km southeast of Utqiagvik (71.285°N, 156.575°W; Figure 1). The

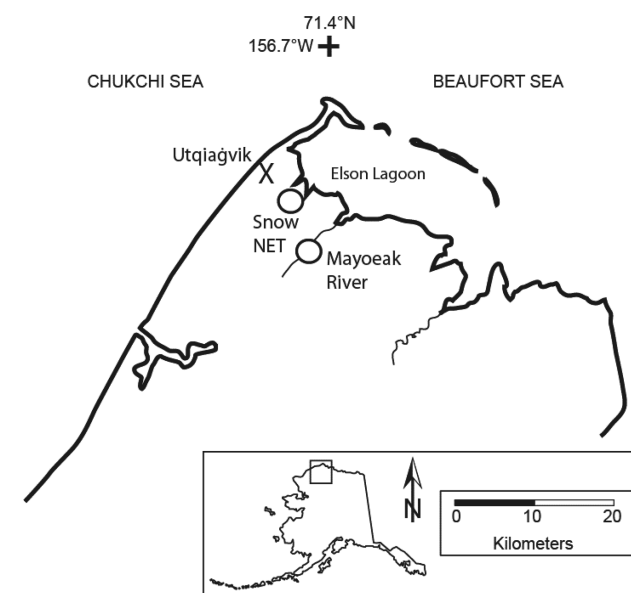


Figure 1. A map of the study site identifying the location of sample collections and the physiography of the area.

site, in the Barrow Environmental Observatory, is far from any major infrastructure, is underlain by continuous permafrost hundreds of meters thick, and has a low topographic relief with high and low centered ice wedge polygons.³⁷ Soils are gelifols with a thin (5 cm) surface mat of sedges over a 2 m thick ice-rich organic peat layer above silty clays and silty loams.³⁸ The small (2.5 ha) experimental catchment drains eastward into Elson Lagoon, which is connected to the Arctic Ocean.

At our study site near Utqiagvik we collected samples of the integrated snowpack, meltwater percolating downward through the snowpack, and surface runoff over frozen tundra. We previously published Hg concentrations and isotopic compositions of atmospheric Hg(0),³¹ fresh snowfall,^{2,36} surface and

Table 1. A Summary of the Mercury Concentrations and Stable Isotope Values from This and Related Studies

sample description	Hg concentration (ng l ⁻¹)	Hg concentration (ng g ⁻¹)	$\delta^{200}\text{Hg}$ (‰)	2σ (‰)	$\delta^{201}\text{Hg}$ (‰)	2σ (‰)	$\delta^{200}\text{Hg}$ (‰)	2σ (‰)	$\delta^{199}\text{Hg}$ (‰)	2σ (‰)	$\Delta^{201}\text{Hg}$ (‰)	2σ (‰)	$\Delta^{200}\text{Hg}$ (‰)	2σ (‰)	$\Delta^{199}\text{Hg}$ (‰)	2σ (‰)
UM-Almadén standard			-0.53	0.16	-0.44	0.13	-0.26	0.08	-0.15	0.08	-0.04	0.08	0.01	0.03	-0.02	0.06
NIST SRM 3133 (snow process standard)			-0.16	0.17	-0.14	0.19	-0.09	0.11	-0.07	0.12	-0.02	0.07	-0.01	0.03	-0.03	0.09
5/28/08 initial melt at the base of the snowpack	32.4		-1.53		-1.57		-0.85		-0.77		-0.42		-0.08		-0.38	
6/1/08 meltwater	25.1		-1.65		-1.58		-0.92		-0.78		-0.34		-0.09		-0.36	
6/9/08 isothermal snowpack- 10 cores	10.2		-1.03		0.91		-0.53		-0.25		-0.13		-0.01		0.01	
6/10/08 Mayoak River vegetation mat (~5 cm)	9.2	319.73	-1.29		-1.05		-0.66		-0.48		-0.08		-0.01		-0.15	
peat at 10.7 cm		77.02	-1.44		-1.47		-0.69		-0.69		-0.39		0.03		-0.33	
peat at 21.4 cm		62.66	-1.13		-1.06		-0.60		-0.48		-0.21		-0.03		-0.19	
peat at 46 cm- depth of typical seasonal thaw		80.17	-1.2		-1.04		-0.62		-0.44		-0.14		-0.02		-0.14	
peat at 63 cm- permafrost			-1.23		-1.00		-0.55		-0.37		-0.08		0.07		-0.06	
peat at 88 cm- permafrost		82.48	-1.39		-1.15		-0.70		-0.40		-0.11		0.00		-0.05	
peat at 140 cm- permafrost		66.17	-1.31		-1.02		-0.54		-0.36		-0.04		0.12		-0.03	
peat at 154 cm- permafrost			-0.81		-0.62		-0.32		-0.18		-0.01		0.08		0.02	
atmospheric Hg(0) ^a			-1.21		-1.04		-0.61		-0.37		-0.13		-0.01		-0.07	
atmospheric Hg(0) ^a			-0.12		-0.13		-0.17		-0.14		-0.04		-0.11		-0.11	
March 2006 recent snowfall ^a	360		0.15		0.12		0.06		-0.18		0.01		-0.01		-0.22	
March 2006 recent snowfall ^a	416		0.54		-0.38		0.19		-0.81		-0.79		-0.08		-0.95	
March 2006 snowpack surface ^a	199		-0.05		-1.23		-0.02		-1.21		-1.19		0.00		-1.20	
March 2006 snowpack surface ^a	81.2		0.70		-1.71		0.24		-2.23		-2.24		-0.12		-2.41	
March 2006 snowpack surface ^a	85.1		-0.10		-2.45		-0.04		-2.52		-2.38		0.01		-2.49	
March 2009 recent snowfall ^b	69.7		-0.49		-2.77		-0.26		-2.40		-2.40		-0.01		-2.63	
March 2009 recent snowfall ^b	88		0.69		-0.48		0.24		-0.83		-1.00		-0.11		-1.01	
atmospheric Hg(0) ^c			0.63		-0.40		0.30		-0.81		-0.88		-0.02		-0.97	
atmospheric Hg(0) ^c			0.71		0.31		0.30		-0.05		-0.22		-0.05		-0.23	
atmospheric Hg(0) ^c			0.70		0.32		0.32		-0.01		-0.21		-0.04		-0.19	
atmospheric Hg(0) ^c			0.55		0.20		0.20		-0.10		-0.21		-0.08		-0.23	
atmospheric Hg(0) ^c			0.58		0.18		0.25		-0.12		-0.26		-0.04		-0.26	
atmospheric Hg(0) ^c			0.69		0.35		0.26		-0.10		-0.17		-0.09		-0.28	
atmospheric Hg(0) ^c			0.80		0.45		0.33		-0.08		-0.15		-0.07		-0.28	

^aSherman et al., 2010. ^bSherman et al., 2012. ^cObrist et al., 2017.

aged snow,¹¹ and peat cores³⁹ from the same area. Detailed sampling information is provided in the Methods section.

2.2. Sample Collection. All snowpack and water sampling materials and Teflon bottles were cleaned in a metal-free clean laboratory using acetone, Citrinox soap, nitric acid, and BrCl followed by five deionized water rinses. Bottles were double sealed in cleaned acid-washed polypropylene bags. Water samples were drawn into cleaned high density polyethylene (HDPE) syringes and collected into poly(tetrafluoroethylene) (PTFE; Teflon) 250 mL bottles (total mercury) and 1 L jars (mercury stable isotopes); all water and snow samples were frozen immediately following collection.

On May 28, 2008, meltwater samples were collected at the base of a small (2 m × 1 m) trench excavated through the 15 cm deep snowpack. Extensive care was taken to ensure the snowpack and snowmelt water samples did not include snow or meltwater that had been in contact with the underlying tundra vegetation. A thin, acid-cleaned 2 m² Teflon sheet was slid gently horizontally between the vegetation surface and the base of the snowpack so we could collect only meltwater percolating through the snowpack prior to it interacting with vegetation or soils. Snowmelt water actively pooling onto the Teflon sheet was collected on May 28 and June 1. It took ~20 min to fill a 1 L sample bottle.

To sample the integrated snowpack on June 9 we used a 10 cm diameter polyvinyl chloride tube with a serrated end that was rotated gently downward into the snowpack to a Teflon scoop inserted into the snowpack following previously described methods.²⁷ The corer was inserted gently from the surface to the base of the snowpack ensuring no layers were preferentially collected or excluded. Snow around the corer was removed with an HDPE shovel and a clean HDPE scoop was slid under the base of the corer to ensure it did not come in contact with the underlying vegetation. The corer was then tipped upside down; 10 of these cores collected 1 m apart from one another to represent a 10 m² area were combined into one cleaned 3 L Teflon sample bottle.

Surface runoff was collected from the Mayoek River (19 km² drainage basin) at a location 5 km southeast of the study watershed on June 10 into 250 mL (total Hg) and 1 L (Hg stable isotopes) cleaned Teflon bottles. The terrain, vegetation, and snowpack of the Mayoek River watershed are similar to the smaller experimental watershed nearby. Our samples were analyzed for total Hg and mercury stable isotope ratios ($\delta^{202}\text{Hg}$, $\Delta^{199}\text{Hg}$, $\Delta^{200}\text{Hg}$, $\Delta^{201}\text{Hg}$, $\Delta^{202}\text{Hg}$, and $\Delta^{204}\text{Hg}$; Table 1). Methods for sample container cleaning and sample collection for the analysis of Hg concentrations and isotopic compositions have been published previously.^{12,36,40}

In July 2008 we collected a shallow (30 cm) sample of the vegetation mat and upper soil from the center of a high centered ice wedge polygon using a clean serrated ceramic knife. This represents the “active layer” above the permafrost that thaws in the summer. In addition, we used a CRREL/Snow, Ice, and Permafrost Research Establishment (SIPRE) 8 cm diameter corer to collect a full 1.5 m core from the SnowNET site in late Oct 2008. Both cores were divided into 10 to 20 cm long sections, placed into cleaned acid-washed polypropylene bags, and immediately frozen.

2.3. Mercury Concentration Analyses. Samples were shipped frozen to the University of Michigan, where they were thawed. Water samples were oxidized with concentrated BrCl to 1% by volume. All mercury analyses were performed by cold vapor atomic absorption spectroscopy using an automated

Nippon Instruments MA-2 mercury analyzer. BrCl in water samples was reduced with NH₂OH and then Hg(II) was reduced with SnCl₂ to Hg(0), concentrated on a gold trap, and released by heating to the detector for analysis. The detection limit for water samples was 0.2 ng/L, and the analytical uncertainty was ±5% for concentration measurements above 1 ng/L. Field and laboratory procedural blanks were collected and analyzed to determine the potential for contamination of samples. Blank checks using 18 MΩ deionized water placed in sample bottles in the field yielded mercury concentrations from 1.1 to 2.1 ng/L, while blanks from snow collection trays ranged from 1.2 to 3.4 ng/L. These blank values are very low compared to the values measured in most samples. In the lowest concentration samples measured, however, the blank is as high as 12% of the Hg in the sample. The spatial variability of mercury deposition to snow is not well-known. When sampling snow in duplicate we collected two samples ~0.5 m apart. During previous sampling campaigns we sampled in triplicate with ~0.5 m lateral spacing between samples. The percent relative standard deviation (%RSD) of the mercury concentrations measured from duplicate samples averaged 9.5%. On all of our data figures the %RSD is smaller than the size of the plotted symbols. Peat samples were sectioned into 1 cm slices in the laboratory, and then both peat samples and the vegetation mat above them were freeze-dried and ground to a powder using a mortar and pestle. Subsamples were combusted in air in a Nippon Instruments MA-2 mercury analyzer. Solid sample detection limits were 0.2 ng/g with an uncertainty of ±5%.

2.4. Mercury Isotope Ratio Measurements. After Hg concentration analysis, water and snow samples with sufficient Hg for isotopic analysis (i.e., >8 ng) were concentrated into acidic 1% KMnO₄ (w/w) solutions as follows. Each sample was poured into a 2 L Pyrex bottle, and 0.3 mL of 30% NH₂OH HCl (w/v) was added and allowed to react for 30 min. A peristaltic pump and Hg-free tubing were then used to add 100 mL of 5% SnCl₂ (w/v) to the solution at a rate of 10 mL/min. Mercury-free air was pulled through the sample and carried the resulting GEM into the KMnO₄ trapping solution at a rate of 0.7 L/min for 4 h. Procedural standards (25 to 50 ng of SRM 3133 in 1% BrCl) and blanks were processed in the same manner. Mercury in these standards was consistently recovered in the final solutions (mean recovery = 91 ± 6%). The small amount of Hg measured in the procedural blanks (mean = 0.22 ± 0.12 ng per blank, *n* = 3) was attributable to the KMnO₄ solutions.

The isotopic composition of Hg in peat samples was measured by combusting the samples in oxygen in a two-stage furnace and then trapping the released Hg(0) in an oxidizing acidic 1% KMnO₄ (w/w) solution. KMnO₄ solutions containing Hg from water, snow, peat, and vegetation samples were adjusted to a concentration of 5 ng/g and measured using continuous-flow cold vapor generation multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) with thallium mass bias correction and sample-standard bracketing to 5 ng/g NIST 3133 standard solutions. Analytical results and uncertainties for internal and external standards are given in Table 1 and agree with literature values.²⁹ Additional details of Hg isotopic analyses have been published elsewhere.^{31,37,41}

3. RESULTS AND DISCUSSION

There is a variety of different types of samples from our study site near Utqiagvik that we analyzed for Hg isotope ratios

including $\delta^{202}\text{Hg}$ (MDF) and $\Delta^{199}\text{Hg}$ (MIF) and that are enclosed in ovals on Figure 2. Some of these analyses were

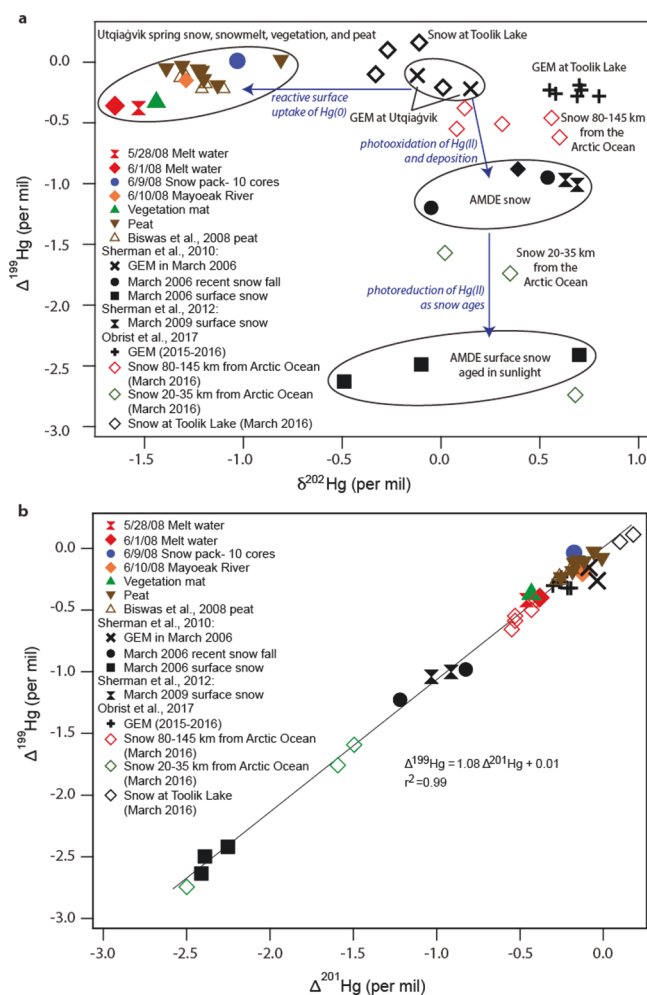


Figure 2. Hg stable isotope composition of ecosystem sources and sinks including snow and GEM from three related studies^{12,13,31} and, from this study, 2008 snowmelt, the surface vegetation mat, and peat from our soil core and from another study in the area.³⁹ (a) Mass-independent ($\Delta^{199}\text{Hg}$) and mass-dependent ($\delta^{202}\text{Hg}$) mercury isotope values with ovals to identify some sample-type groupings and (b) mass-independent Hg isotopic compositions ($\Delta^{199}\text{Hg}$ and $\Delta^{201}\text{Hg}$).

presented in previous publications by us.^{12,31,39} We also include analyses of GEM and snow from Obrist et al.¹³ from Toolik Lake (~200 km south of the Arctic Coast) and along a transect from Toolik to the Arctic Coast, to provide additional analyses of GEM and snow on the north slope of Alaska (these samples are not enclosed in ovals on Figure 2). Samples analyzed by us from near Utqiagvik include: GEM (March), fresh snowfall (March), aged snow (March), integrated snowpack (May/June), snowpack meltwater (May/June), surface runoff during the melt period (June), surface vegetation mat (October), and a 150 cm profile of peat (Oct). Snow samples collected in 2006 and 2009, for which we also have Hg stable isotope measurements, range in total Hg concentrations from 69 to 416 ng/L. These Hg concentrations are more than 30 times greater than the highest concentration reported from inland snow at Toolik Lake.¹³ Initial meltwater at the base of the snowpack (32.4 ng/L), meltwater on June 1 (25.1 ng/L),

the integrated snowpack (10.2 ng/L), and the Mayoeak River (9.2 ng/L) all yield lower concentrations.

Among the samples we analyzed from Utqiagvik there is a wide range in both $\delta^{202}\text{Hg}$ and $\Delta^{199}\text{Hg}$ values. Relative to other sample types, GEM has high $\delta^{202}\text{Hg}$ (near zero) and high $\Delta^{199}\text{Hg}$ (averaging -0.1‰). March fresh snowfall collected during active AMDEs at Utqiagvik has high $\delta^{202}\text{Hg}$ similar to GEM but with much lower $\Delta^{199}\text{Hg}$ averaging -1.1‰ . GEM measured at Toolik Lake has a $\sim 0.7\text{‰}$ greater $\delta^{202}\text{Hg}$ value than GEM measured at Utqiagvik, and the two populations are statistically significantly different (using an analysis of means with a significance level (α) of 0.05). The $\Delta^{199}\text{Hg}$ values at both sites are statistically significantly indistinguishable but the two Utqiagvik samples are slightly higher than those from Toolik Lake. Aged snow from the March AMDE season has $\delta^{202}\text{Hg}$ similar to fresh snow but with a much lower $\Delta^{199}\text{Hg}$ averaging -2.5‰ . Finally, there is a large contrast between the isotopic composition of Hg in all of the March snow samples from Utqiagvik and the isotopic composition of Hg in all of the May/June snowpack and snowmelt samples (Figure 2a).

All of the snowmelt samples from Utqiagvik display MDF and MIF similar to the June snowpack. May/June snowpack and meltwaters have $\Delta^{199}\text{Hg}$ near zero (average -0.16‰), like GEM, but have $\delta^{202}\text{Hg}$ 1.0 to 1.5‰ lower than GEM and March snow. On a $\Delta^{199}\text{Hg}$ vs $\Delta^{201}\text{Hg}$ plot the samples fall on a line with a slope of ~ 1 , indicative of photochemical reduction of Hg(II) (Figure 2b). Hg in the vegetation mat and the upper 5 cm of peat has $\delta^{202}\text{Hg}$, $\Delta^{199}\text{Hg}$, and $\Delta^{201}\text{Hg}$ values that overlap with values for the May/June snow and snowpack, meltwater, and Mayoeak River runoff samples that we ascribe to Hg released by melting of the seasonal snowpack.

The peat samples provide a long-term archive of the Hg stable isotope values deposited to the study area during all seasons. Figure 3a includes Hg concentrations for the peat cores, and the Hg stable isotope values are provided in Figure 3b. In each of two cores the surface vegetation mat Hg concentrations are ~ 3 times that of the peat soils below. In earlier work from similar samples at this research site near-surface peat samples with elevated Hg concentrations were identified as of “modern age”,³⁹ but neither that study nor this study have age dates to confirm this. $\delta^{202}\text{Hg}$ and $\Delta^{199}\text{Hg}$ values of the surface vegetation are slightly lower than that of the seasonally thawed soils and permafrost peat. On the basis of a comparison of means with a significance level (α) of 0.05 the $\delta^{202}\text{Hg}$ values of the vegetation and peat are not statistically different, but the $\Delta^{199}\text{Hg}$ values of the vegetation and peat are statistically different. The vegetation and peat $\Delta^{199}\text{Hg}$ and $\delta^{202}\text{Hg}$ values are similar to the snowmelt and runoff values as well as what would be expected for GEM deposition to vegetation during the summer.^{17,32,33} Previous studies have reported that at least 70% of the Hg deposition is attributable to gaseous elemental Hg at Arctic inland¹⁷ and coastal²¹ locations. It is clear from the results of this study that the end of winter Hg deposition to the tundra from melting of the seasonal snowpack has a dominantly atmospheric GEM $\Delta^{199}\text{Hg}$ signature. The $\delta^{202}\text{Hg}$ value of snowmelt is consistent with reactive surface uptake of GEM and is isotopically similar to what would be expected from reactive surface uptake onto vegetation surfaces or the snowpack.

Our interpretation of the contrasting Hg isotope ratios among the five different types of samples we analyzed near Utqiagvik (Figures 2 and 3) is based on current knowledge of

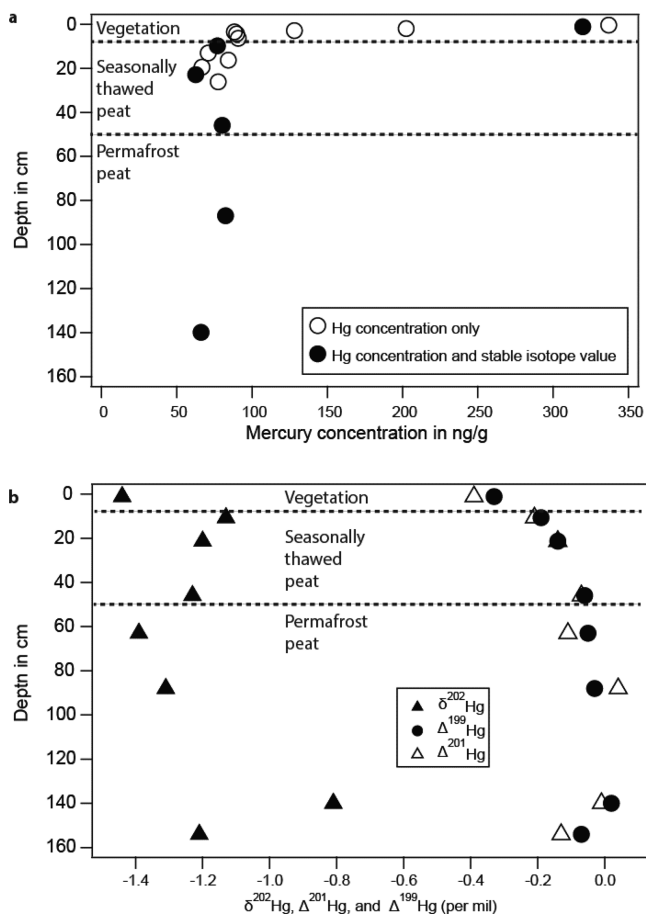


Figure 3. Mercury concentrations and mercury stable isotope values from a late summer sampling event representing the seasonally thawed layer above permafrost (open circles in (a)) and from a 1.5 m core collected in the late spring when the ground was frozen (closed circles in (a)) and all symbols in (b)).

the Hg isotope fractionations known to occur during important Hg transformations in the atmosphere and during deposition to the land surface.^{29,42} The isotopic composition of GEM in the Arctic near Utqiagvik is similar to values measured at numerous lower latitude locations³² and at Toolik Lake.¹³ For example, the GEM $\Delta^{199}\text{Hg}$ values for Toolik Lake and Utqiagvik are within 0.25 ‰ of one another, while GEM $\delta^{202}\text{Hg}$ values for Toolik Lake and Utqiagvik are within 1 ‰ of one another. GEM values for $\Delta^{199}\text{Hg}$ and $\delta^{202}\text{Hg}$ measured in the Great Lakes Region³² also fall within the range for Toolik Lake and Utqiagvik. During March AMDEs, Hg(0) is photochemically oxidized in the lower atmosphere and deposited to snow and ice surfaces.^{9,36,43} We suggest, on the basis of previous studies, that this snow has similar $\delta^{202}\text{Hg}$ as GEM but with lower $\Delta^{199}\text{Hg}$ than GEM due to fractionation from photochemical oxidation of Hg(0) to Hg(II) in the atmosphere.^{12,40} Once this Hg(II) is deposited to the snowpack, some of the Hg(II) is photochemically reduced as the snow ages, further driving the remaining Hg(II) in surface snow to the progressively lower $\Delta^{199}\text{Hg}$ values we observed for the surface of drifted snow in March (prior to initiation of the melt; Figure 2a). The average $\Delta^{199}\text{Hg}$ of GEM we measured is -0.16 ‰, and the average of fresh snow we sampled had $\Delta^{199}\text{Hg}$ of ca. -1.04 ‰. The surface of aged snow had even lower $\Delta^{199}\text{Hg}$ of ca. -2.5 ‰. These three different sample types yield statistically different $\Delta^{199}\text{Hg}$ values based on an

analysis of means with a significance level (α) of 0.05. All of the snow samples collected during the spring AMDE season had high $\delta^{202}\text{Hg}$ values between -0.5 and 0.7 . In striking contrast, May and June snow cores (representing periods when AMDEs were no longer active), meltwaters, the vegetation mat, and near-surface peat samples have much lower $\delta^{202}\text{Hg}$ values of -1.3 and -1.1 ‰, but $\Delta^{199}\text{Hg}$ values near zero—matching that of GEM. As mentioned above, the vegetation, peat, and spring AMDE snow from Utqiagvik have $\Delta^{199}\text{Hg}$ values in the same range as soils and vegetation from Toolik Lake.¹³

Obrist et al. (2017)¹³ concluded that the shift in $\delta^{202}\text{Hg}$ to lower values in soils and vegetation compared to GEM was caused by isotopic fractionation during reactive surface uptake of GEM by vegetation by a process that was documented previously.³² This interpretation is plausible for the Toolik Lake study, but it cannot explain the offset in $\delta^{202}\text{Hg}$ between GEM and May/June snow and meltwater that has not come in contact with vegetation or soil that we observe in Utqiagvik. We suggest instead that GEM is being oxidized and retained within the snowpack at Utqiagvik through a reactive surface uptake process mediated by halogens^{14,15,17,18,25,42,44} and/or by organic matter, which is known to be present in Arctic snow.²⁴ This is somewhat analogous to GEM entering the stomata of leaves and becoming oxidized by organic matter within the foliage.³² During the summer months GEM may also be oxidized and fractionated by vegetation and soil at Utqiagvik by the same process observed at Toolik Lake.¹³

Thus, we identified one characteristic Hg isotope signature for Hg deposited during AMDEs (with high $\delta^{202}\text{Hg}$ and a range of $\Delta^{199}\text{Hg}$ values depending on the degree of photoreduction and release of Hg(0) from the snowpack) and another, which we hypothesize to be for Hg deposited by GEM within the snowpack (with low $\delta^{202}\text{Hg}$ and high $\Delta^{199}\text{Hg}$). Snow deposited during the March AMDE season has a similar $\delta^{202}\text{Hg}$ value as atmospheric GEM. The snowpack during the May/June snowmelt season has a highly contrasting Hg isotopic signature compared to the March snowpack, and it is shifted by ~ 2 ‰ to lower $\delta^{202}\text{Hg}$ by oxidation of GEM in the snowpack. Since the isotopic composition of meltwater overlaps that of the snowpack we conclude that virtually all of the Hg released in meltwater during the spring melt is derived from Hg that originated as GEM and was deposited to the snowpack by oxidation and reactive surface uptake within the snowpack. In contrast, Hg deposited to snow crystals during AMDEs at high concentrations is largely photochemically reduced and released back to the atmosphere as GEM, leaving low concentrations (ca. fourfold lower; see Table 1) of residual Hg(II) with a similar $\delta^{202}\text{Hg}$ as GEM, but a much lower $\Delta^{199}\text{Hg}$, as has been observed for AMDEs following photoreduction in aged snow.³¹ Because the Hg(II) is deposited within the snowpack its exposure to sunlight is dependent on the light penetration depth, often quantified by the e-folding depth, which is the depth at which irradiance is attenuated to 37% of its initial value. This has been measured at Utqiagvik to be between 3 and 18 cm depending on the snow type and wavelength.⁴⁵ As such, we would expect the oxidation of Hg in the snowpack to be dominated by processes occurring in the upper ~ 15 – 20 cm.¹⁸ In late spring, during snowmelt, as the snowpack degrades and shrinks, the penetration depth of sunlight likely increases as a percentage of the total snowpack depth because of an increase in grain size.⁴⁶

Previous studies have suggested that ~75% of the Hg deposited during AMDEs is photochemically reduced from snow and re-emitted to the atmosphere.^{21,31} A small amount of AMDE-derived Hg may be present in snowmelt, but based on the average $\Delta^{199}\text{Hg}$ of GEM (-0.16‰), the average $\Delta^{199}\text{Hg}$ of AMDE derived Hg (-1.04‰), and the $\Delta^{199}\text{Hg}$ of spring snowmelt (-0.37‰), we calculate from our data, using a simple mixing model, that it comprises a maximum of 24% of the total Hg. The proportion of AMDE Hg in snowmelt could be as low as 9% if the AMDE Hg endmember is taken to be Hg in AMDE-deposited snow that has been aged in sunlight, lowering its $\Delta^{199}\text{Hg}$ to an average of -2.51‰ (Figure 2a). Thus the dominant source of the Hg in our spring melt samples is GEM that has been oxidized by reactive halogens and/or organics within the snowpack. Enhanced concentrations of GEM in the arctic coastal atmosphere have been observed at the start of the snowmelt period.⁹ The enhanced GEM and its oxidation and retention in the snowpack provides an explanation for the higher Hg concentrations in coastal snow, snow on sea ice, and snowmelt compared to inland locations on the Arctic Coast.

Projected future warming in the Arctic will produce a more dynamic sea ice regime. This includes a decline in sea ice extent, an increasing fraction of first year ice, and an increasing areal extent of open sea-ice leads.^{47,48} These conditions are expected to provide a greater pool of reactive halogens to coastal snowpacks and this may promote GEM oxidation and deposition into the snowpack. Further research, in both laboratory and field settings, is needed to explore the links between snowpack halogens and Hg oxidation and retention in the snowpack. Additionally, there is an increasing need to better account for the spatial and temporal variability of Hg deposition and oxidation and the role of AMDEs and halogen-rich snow in Hg deposition across the entire Arctic region.

ACKNOWLEDGMENTS

This work was funded by the U.S. National Science Foundation Office of Polar Programs Grant Nos. ARC-0435989 (U.S. Army Cold Regions Research and Engineering Laboratory) and ARC-0435893 (Univ. of Michigan). Extensive logistical support was provided by the Barrow Arctic Science Consortium, and their assistance is greatly appreciated. Numerous colleagues assisted with sample collection and hearty discussions of the Arctic mercury cycle, particularly M. Sturm, C. Polashenski, A. Steffen, and L. Sherman. We thank anonymous reviewers for their comments on earlier versions of the manuscript.

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1. REPORT DATE (DD-MM-YYYY) June 2021		2. REPORT TYPE Final		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE Mercury Isotopes Reveal Atmospheric Gaseous Mercury Deposition Directly to the Arctic Coastal Snowpack				5a. CONTRACT NUMBER	
				5b. GRANT NUMBERS ARC-0435989 and ARC-0435893	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Thomas A. Douglas and Joel D. Blum				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army Engineer Research and Development Center Cold Regions Research and Engineering Laboratory 72 Lyme Road Hanover, NH 07552				8. PERFORMING ORGANIZATION REPORT NUMBER ERDC/CRREL MP-21-5	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. National Science Foundation Office of Polar Programs Alexandria, VA 22314				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.					
13. SUPPLEMENTARY NOTES Originally published by the American Chemical Society in the <i>Environmental Science and Technology Letters</i> on 7 March 2019.					
14. ABSTRACT Springtime atmospheric mercury depletion events (AMDEs) lead to snow with elevated mercury concentrations (>200 ng Hg/L) in the Arctic and Antarctic. During AMDEs gaseous elemental mercury (GEM) is photochemically oxidized by halogens to reactive gaseous mercury which is deposited to the snowpack. This reactive mercury is either photochemically reduced back to GEM and re-emitted to the atmosphere or remains in the snowpack until spring snowmelt. GEM is also deposited to the snowpack and tundra vegetation by reactive surface uptake (dry deposition) from the atmosphere. There is little consensus on the proportion of AMDE-sourced Hg versus Hg from dry deposition that is released in spring runoff. We used mercury stable isotope measurements of GEM, snowfall, snowpack, snowmelt, surface water, vegetation, and peat from a northern Alaska coastal watershed to quantify Hg sources. Although high Hg concentrations are deposited to the snowpack during AMDEs, we estimate that ~76 to 91% is released back to the atmosphere prior to snowmelt. Mercury deposited to the snowpack as GEM comprises the majority of snowmelt Hg and has a Hg stable isotope composition similar to Hg deposited by reactive surface uptake of GEM into the leaves of trees in temperate forests. This GEM-sourced Hg is the dominant Hg we measured in the spring snowpack and in tundra peat permafrost deposits.					
15. SUBJECT TERMS Arctic regions, Snow, Mercury—Isotopes, Atmospheric deposition					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT SAR	18. NUMBER OF PAGES 13	19a. NAME OF RESPONSIBLE PERSON
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (include area code)