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## Journal Article

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# Fate of springtime atmospheric reactive mercury: Concentrations and deposition at Zeppelin, Svalbard

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## KEYWORDS:

Aerohead, Arctic, Pollution, RMAS, Speciation, Thermal desorption

1 **Abstract**

2 Mid-latitude atmospheric elemental mercury (Hg) emissions undergo extensive oxidation to reactive  
3 Hg (RM) compounds during Arctic polar sunrise, resulting in enhanced atmospheric deposition that  
4 impacts Arctic marine wildlife and humans. It has been difficult to estimate RM dry deposition,  
5 because RM concentrations, compounds, and their deposition velocities are ill-defined. Here we  
6 investigate RM concentrations sampled with membrane-based methods, and find these to exceed  
7 denuder-based RM detection by 5 times at the Zeppelin Observatory on Svalbard (March 26 – July 24,  
8 2019). Measured dry deposition of GOM was about half of modeled RM deposition demonstrating  
9 that particulate-bound Hg was an important component of dry deposition. Using thermal membrane  
10 desorption RM chemistry was found to be dominated by Hg–Cl/Br (51%) and Hg–N (45%)  
11 compounds. Back trajectory analysis indicated that Hg–Br/Cl compounds were predominantly  
12 advected from within the marine boundary layer (sea ice exposure), while Hg–N originated from the  
13 free troposphere. Weekly average RM compound-specific dry deposition velocities ranged from 0.12  
14 to 0.49 cm s<sup>-1</sup>, with a net RM dry deposition of 1.9 μg m<sup>-2</sup> (1.5 – 2.5 μg m<sup>-2</sup>; 95% confidence interval),  
15 that exceeds the mean annual Hg wet deposition flux in Svalbard. Overall, we find that springtime  
16 atmospheric RM deposition has been underestimated in the Arctic marine environment.

**SYNOPSIS:**

Atmospheric reactive mercury measurements at Svalbard demonstrate elevated deposition to Arctic ecosystems (5.6-times), and input of Hg-N and halogenated compounds.

## 17 1. Introduction

18 Mercury (Hg) pollution in the Arctic is of concern, because indigenous people rely heavily on marine-  
19 based diets that expose them to neurotoxic methylmercury<sup>1,2</sup>. Globally, the toxic burden of  
20 anthropogenic Hg pollution for human and ecosystem health is accepted by policy makers, and has  
21 resulted in the UNEP Minamata Convention that aims to reduce human and ecosystem exposure to  
22 Hg<sup>3</sup>. However, to evaluate the effectiveness of the Convention we must improve our understanding on  
23 how Hg cycles between air, land, water, ice, and snow, especially in vulnerable ecosystems, such as  
24 the Arctic<sup>4</sup>. The uncertainty in estimates of atmospheric Hg deposition as gaseous elemental Hg  
25 (GEM), gaseous oxidized Hg (GOM), or as particulate-bound Hg (PBM) to the Arctic Ocean is  
26 illustrated by a comparison of two global numerical Hg models. The GEOS-Chem model<sup>4</sup> suggested  
27 an atmospheric Hg input to the Arctic Ocean of 76 Mg yr<sup>-1</sup>, while the GRAHM model estimated 108  
28 Mg yr<sup>-1</sup><sup>5</sup>.

29 The discovery of coastal springtime atmospheric Hg depletion events (AMDEs) in 1995 indicated that  
30 reactive Hg (RM = GOM + PBM) dry deposition was an important pathway for atmospheric Hg inputs  
31 to Arctic marine ecosystems<sup>6</sup>. Subsequent studies suggested that during AMDEs about 100 Mg RM yr<sup>-1</sup>  
32 <sup>1</sup> was deposited to Arctic snow and ice<sup>7,8</sup>. Oxidation of GEM to GOM during AMDEs is primarily  
33 induced by photochemical activation of sea ice-derived halogen compounds<sup>8,9</sup>. In particular, bromine  
34 oxide and atomic bromine radicals (BrOx, BrO, Br•) lead to the destruction of ozone (O<sub>3</sub>) and  
35 oxidation of GEM, with subsequent depletion of both GEM and O<sub>3</sub> in the Arctic atmosphere during  
36 polar sunrise<sup>10,11</sup>. Most recently, Obrist et al.<sup>12</sup> found that RM dry deposition to coastal Arctic tundra  
37 was substantial during springtime AMDEs, depositing 0.8 – 2.8 µg m<sup>-2</sup> yr<sup>-1</sup>. Dry deposition of RM  
38 during AMDEs results in higher total Hg concentrations in snow<sup>13,14</sup> that can be followed by re-  
39 emission of Hg<sup>0</sup> after photo-reduction<sup>2,15,16</sup>. Approximately 90% of the total Hg in snow can be re-  
40 emitted back to the atmosphere after AMDEs<sup>1</sup>.

41 To assess the total input of Hg to Arctic ecosystems during AMDEs, it is crucial to improve RM dry  
42 deposition estimates. This could be done by measuring ambient RM concentrations and applying the  
43 values in dry deposition models or identifying RM compounds in ambient air and applying compound-  
44 specific deposition velocity calculations based on local meteorological data. The spatial resolution of  
45 Arctic RM measurements is limited, and the widely used measurement technique to quantify  
46 atmospheric Hg (Tekran® speciation system [Tekran® 2537/1130/1135]; Tekran® Instrument Corp.,  
47 Ontario, Canada) has been demonstrated to underestimate RM by a factor of 2 to 13 in the planetary  
48 boundary layer<sup>17-24</sup>, and by a factor of 1.6 in the free troposphere<sup>25</sup>. Other studies suggest measurement  
49 artefacts for PBM are generated by temperature and collection time<sup>26-28</sup>. Selective collection and  
50 analysis of particles smaller than 2.5 µm diameter with the Tekran® also raises the question of the  
51 possible underestimation of PBM concentrations<sup>29</sup> particularly in oceanic environments where the RM  
52 compounds are dominantly associated with larger (2 – 10 µm) marine aerosols<sup>30,31</sup>.

53 The University of Nevada, Reno – Reactive Mercury Active System 2.0 (RMAS), with cation  
54 exchange membranes (CEM) and nylon membranes<sup>32</sup>, in combination with a down-facing  
55 aerodynamic sampler housing that also uses CEMs (Aerohead sampler)<sup>33,34</sup>, have been shown to  
56 improve RM concentration measurements, and GOM and RM dry deposition estimates, respectively,  
57 relative to the Tekran® 2537/1130/1135 system<sup>35</sup>. These measurement methods have never been  
58 applied in the Arctic, though they are necessary since a low bias in RM deposition would lead to  
59 underestimation of Hg transfer from the atmosphere to marine and terrestrial ecosystems during  
60 AMDEs. Using the RMAS, the chemistry of RM compounds can be suggested using thermal  
61 desorption of nylon membranes and subsequent peak deconvolution<sup>20,21,32,36</sup>. This methodology allows  
62 for understanding if specific compounds namely HgO, Hg-Br/Cl (e.g. HgBr<sub>2</sub>, HgCl<sub>2</sub>), Hg-nitrogen  
63 (e.g., Hg(NO<sub>3</sub>)<sub>2</sub>), and Hg-sulfur (e.g., HgSO<sub>4</sub>), as well as some organic-bound compounds (e.g.,  
64 MeHg)<sup>24</sup> are present. Knowledge about the chemistry of RM improved local estimates of RM  
65 deposition at a coastal research site in Florida, USA<sup>36</sup>. Estimates of dry deposition were based on  
66 compound-specific deposition velocity calculations using a multiple resistance model that was  
67 developed by Zhang et al.<sup>37</sup> and modified by Lyman et al.<sup>33</sup>.

68 Explaining the bias in atmospheric RM concentration among different measurement methods, in  
69 combination with better identification of chemical compounds of RM, has been identified as a top  
70 priority task to improve the determination of RM dry deposition from local to global scales<sup>18</sup>. Here we  
71 present a procedure to determine RM compound-specific dry deposition velocities in order to calculate  
72 springtime RM dry deposition in the Ny-Ålesund area on Svalbard. The goals of the study were to: 1)  
73 intercompare RM concentrations using automated (Tekran®) and manual methods (RMAS); 2)  
74 identify RM compounds by thermal desorption procedures; 3) investigate the source of RM  
75 compounds using back-trajectory analysis; and 4) calculate RM compound-specific dry deposition  
76 velocities and compare them with dry deposition measurements made by the Aerohead sampler. The  
77 incorporation of new observations of RM concentration, chemistry and compound-specific dry  
78 deposition velocities is a necessary intermediate step toward substantially improving numerical  
79 models of Hg cycling in the Arctic.

## 80 **2. Material and Methods**

### 81 **2.1 Location and sampling**

82 Air measurements were carried out from March 26 (11:00) to July 24 (08:00), 2019 at the Zeppelin  
83 Observatory (Zeppelin), located on Svalbard in the Norwegian Arctic. The atmospheric research and  
84 monitoring station was located on Zeppelin Mountain at 474 m a.s.l. (78.90°N, 11.88°E). The  
85 observatory was situated far from major air pollution sources, and thus, was within an undisturbed  
86 Arctic environment. A steep downhill slope faced north towards the research village of Ny-Ålesund, a  
87 small settlement with 35 to 185 inhabitants at 2 km from the sampling site. The station was operated  
88 by the Norwegian Institute for Air Research (NILU) in close collaboration with the Norwegian Polar  
89 Institute (NPI). Air inlets for all air Hg measurements were installed 3 m above ground in close  
90 proximity to one another, facing downward and toward the predominant wind direction (ESE).  
91 Automated atmospheric Hg measurements were carried out by Norwegian University of Science and  
92 Technology (NTNU) in collaboration with NILU; manual sampling for RM analyzes was performed  
93 by NPI staff. Previous analysis of automated atmospheric Hg and snow Hg measurements at Zeppelin  
94 were reported by Dommergue et al.<sup>13</sup>, Berg et al.<sup>38-40</sup>, Aspino et al.<sup>41</sup>, Gauchard et al.<sup>42</sup>, Sprovieri et  
95 al.<sup>43,44</sup>, Sommar et al.<sup>45</sup>, Ferrari et al.<sup>46</sup>, Steen et al.<sup>47</sup>, and Angot et al.<sup>48</sup>.

### 96 **2.2 Automated GEM and RM measurements**

97 During the campaign, a Tekran® measured GEM, GOM, and PBM continuously following methods  
98 briefly described in section S1 and detailed in Landis et al.<sup>49</sup>. The only deviation from the standard  
99 operation procedures<sup>50,51</sup> was calculating GOM with the flush blank concentrations added to the GOM  
100 measurement; this was done because adding the Tekran® flush blank to RM (GOM + PBM)  
101 measurements resulted in a good agreement with manual RM measurements using polyethersulfone  
102 membranes at the high altitude Pic du Midi Observatory<sup>25</sup>.

### 103 **2.3 Manual RM measurements**

104 Three different sorption surface materials were used to sample RM. Polyethersulfone membrane (PES,  
105 47 mm diameter, 0.45 µm pore size; Millipore) were previously applied<sup>25,52</sup> and showed a similar  
106 sorption capacity and background Hg contents to CEM<sup>53</sup>. The PES and CEM (PES backbone that has  
107 been proprietarily treated, 47 mm diameter, 0.8 µm pore size; Mustang-S, Pall Corporation) were  
108 applied extensively in recent studies (e.g., Gustin et al.<sup>19</sup>; Maruszczak et al.<sup>25</sup>; Luippold et al.<sup>32</sup>, Miller  
109 et al.<sup>54</sup>) and were deemed the preferable material for quantitative RM measurements due to the high  
110 RM sorption efficiency<sup>53</sup>. Nylon membranes (47 mm diameter, 0.2 µm pore size; Sartorius Stedium)  
111 were used to determine the chemistry of RM using thermal desorption procedures<sup>19,24</sup>. The chemistry  
112 of the RM compounds captured on the nylon membranes was determined by comparing membrane Hg  
113 desorption profiles from Svalbard with those developed for standard Hg compounds (see section 2.4  
114 also).

### 115 **2.3.1 PES measurements**

116 The PES sampling configuration captured RM in ambient air by pumping at  $1 \text{ L min}^{-1}$  (Membrane  
117 vacuum pump, KNF) through a one-stage outdoor filter pack protected from snow fall. The airflow  
118 was regulated by a ball flow meter (Fisher Scientific) and quantified with a digital volume meter  
119 (Siargo Ltd.). The flow was regularly checked with a Bios Defender calibration unit and considered  
120 stable throughout the campaign. In the laboratory, the RM content on the PES after digestion was  
121 determined using a Brooks Rand Model III cold vapor atomic fluorescence spectrometer (CVAFS).  
122 The method detection limit (MDL) was  $5 \text{ pg Hg}^{25}$ . Details on RM analysis are described in section S2  
123 and a data overview is given in section S3. In total, eight blank membranes were collected from the  
124 jars that housed the PES prior to deployment of the new samples. The mean Hg content on PES blanks  
125 was  $13 \pm 8 \text{ pg}$  ( $1\sigma$ ,  $n = 8$ ). The limit of detection (LOD) was  $25 \text{ pg}$  ( $3\sigma$  of blank). The lowest RM on  
126 PES was  $333 \text{ pg}$ , collected from June 4 to June 11, 2019. The blank percentage compared to the  
127 median RM was 2% (ranged from 1% to 6%) and all samples were above the LOD.

### 128 **2.3.2 RMAS membrane total Hg measurements**

129 The RMAS was used to collect RM on CEM and nylon membranes. The sampling procedures for  
130 CEM and nylon membranes and their blank treatments were identical. Previous studies showed that  
131 nylon membranes did not collect all ambient compounds with the same efficiency as CEMs<sup>19,53</sup>, but  
132 that the RM chemistry was in good agreement with measurements of anions (e.g.,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ )<sup>24</sup>, and  
133 that RM compounds sorbed to the membrane did not transform during storage and shipment<sup>53</sup>. For RM  
134 sampling, ambient air was drawn through 6 sampling ports ( $n = 3$  CEM,  $n = 3$  nylon) at a flow rate of  
135  $1.7 \pm 0.2 \text{ L min}^{-1}$ . The downstream membranes in the two-stage filter holders allowed for the capture  
136 of Hg that passed through the upstream membrane. A detailed description of the RMAS can be found  
137 in Luippold et al.<sup>24</sup>. Triplicate blank CEM and nylon membranes were collected from the same jars as  
138 those that held the sample membranes. CEM and downstream nylon membranes were digested and  
139 analyzed using CVAFS following EPA Method 1631, and upstream nylon membranes are thermally  
140 desorbed (sections 2.4, S2). The mean of the triplicate CEM blanks, collected weekly at the start of  
141 each deployment, was  $38 \pm 13 \text{ pg}$  ( $1\sigma$ ,  $n = 17$ ), and the mean nylon membrane blank Hg content was  
142  $14 \pm 7 \text{ pg}$  ( $1\sigma$ ,  $n = 17$ ). All CEM samples were above the LOD of  $38 \text{ pg}$  ( $3\sigma$  of blank); the LOD was  
143 less than 5% of the median RM ( $785 \text{ pg}$ ). Median CEM breakthrough for all samples was 8% ( $n = 17$ ).  
144 The nylon membrane LOD was  $20 \text{ pg}$  ( $3\sigma$  of blank); the two last samples of the campaign (harvested  
145 on July 17 and 24, 2019) were below the LOD. The mean breakthrough on the nylon membrane was  
146 2% ( $1\sigma$ ,  $n = 15$ ), excluding the samples below the LOD.

### 147 **2.4 RM compounds**

148 Upstream nylon membranes were thermally desorbed to characterize and quantify RM compounds.  
149 The thermal desorption profiles for different RM compounds (Section S4) were compared to pure  
150 GOM compounds for which profiles have been developed, including  $\text{HgO}$ ,  $\text{HgBr}_2$ ,  $\text{HgCl}_2$ ,  $\text{HgN}_2\text{O}_6$ ,



151 HgSO<sub>4</sub>, and elemental Hg, as well as methylmercury chloride directly added to membranes<sup>20,21,36</sup>.  
152 Thermal desorption profiles have been used to identify Hg compounds not only in ambient air but in  
153 other matrices. Exemplarily, Biester and Scholz<sup>55</sup> developed profiles for solids that have peaks at  
154 similar locations as ours for similar compounds.

155 Individual RM compounds were identified from peak deconvolution of thermal desorption  
156 profiles<sup>19,20,24,32</sup>. Each profile was considered to follow a Gaussian distribution (Section S3) and was  
157 deconvoluted based on the curve fitting function in MATLAB v. 2018a. Peak temperature ranges were  
158 defined for different compounds using an improved calibration system: 80–85 °C for [-O], 90–110 °C  
159 for [-Br/Cl], 125–135 °C for [-N], 150–155 °C for [-S], and 180–190 °C for methylmercury (MeHg) or  
160 generally organic Hg compounds<sup>24,32</sup>. To quantify the RM compounds on each nylon membrane, the  
161 integral of the area beneath each Gaussian peak was calculated (pg·m<sup>-3</sup>·°C). The relative contribution  
162 of each RM compound was calculated based on the integrated peak area. The percentage of the  
163 compounds was determined by dividing the concentration of the identified compound using thermal  
164 desorption data, specifically the area under the curve, by the total amount of RM measured. RM  
165 compound contribution collected on each nylon membrane was determined weekly based on the peak  
166 deconvolution analysis. For details on the thermal desorption and peak deconvolution procedures, see  
167 Luippold et al.<sup>32</sup>.

## 168 **2.5 Back trajectory modeling**

169 The Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT, v. 4.2.0), developed  
170 by NOAA<sup>56</sup>, was driven with 3-hourly meteorological input data from the Global Data Analysis  
171 System (GDAS; 1° latitude-longitude 360 by 181 grid) to identify the potential source regions of RM  
172 compounds. The model was run in backward mode for 10 days every 2 hours throughout the CEM and  
173 nylon membrane sampling periods at Zeppelin (474 m a.s.l.). In total, ~84 backward trajectories were  
174 calculated for each sampling period. The spatial (horizontal and vertical) residence time of the air  
175 masses were calculated. The back trajectory model results were combined with five major surface  
176 categories – land (no snow cover), open water, permanent ice/snow, sea ice, and snow on land,  
177 determined using ESRI ArcGIS Pro (v. 10.6) – to provide the time series of percent surface exposure  
178 of particles along trajectories. Moreover, the percent of particles along trajectories that reside within  
179 the boundary layer (BL) and in the free troposphere (FT) was analyzed. Details on generation of  
180 surface maps and back trajectory statistics are given in section S5.

## 181 **2.6 GOM/RM dry deposition**

### 182 **2.6.1 Dry deposition measurements**

183 Three passive Aerohead samplers were deployed to measure GOM dry deposition<sup>33,34</sup> next to the inlets  
184 for the automated and manual RM samplers. GOM was collected on CEM (127 mm diameter, 0.8 µm  
185 pore size; Mustang-S, Pall Corporation) on a weekly basis. After each deployment, the three CEM and  
186 two non-deployed blanks were collected. The samples were stored in 50 mL centrifuge tubes in

187 double-zipper bags at -20 °C. In the laboratory, the membranes were digested and analyzed identically  
188 to the CEM and nylon from the RMAS. Dry deposition of RM was calculated following Lyman et al.  
189 <sup>34</sup>:

$$190 \quad D = \frac{S-B}{A \cdot T}, \quad (1)$$

191 where D is the deposition rate in ng m<sup>-2</sup> h<sup>-1</sup>, S is the mass of Hg on the membrane (ng), B is the mass  
192 of Hg on the method blanks (ng), A is the surface area of the membrane (0.0104 m<sup>2</sup>), and T is the  
193 deployment duration (h). The mean of all Aerohead CEM blanks was 166 ± 112 pg (1σ, n = 35). The  
194 RM dry deposition MDL for a weekly deployment was 0.29 ng m<sup>-2</sup> h<sup>-1</sup> (blank + 3σ). Uncertainty in the  
195 GOM dry deposition measurements originates from the fact that we measure deposition on an  
196 artificial surface and not on snow, ice or tundra vegetation directly, where GOM can be reduced and  
197 subsequently re-emitted to the atmosphere. The surface of the CEM provides physical means for  
198 understanding temporal changes of GOM dry deposition<sup>34</sup>.

### 199 **2.6.2 Dry deposition modeling**

200 Weekly dry deposition of RM was estimated in a three step procedure. First, we determined the  
201 individual RM compounds (Hg(OH)<sub>2</sub>, HgBr<sub>2</sub>/HgCl<sub>2</sub>, HgN<sub>2</sub>O<sub>6</sub>, HgSO<sub>4</sub>, MeHg) using thermal  
202 desorption and peak deconvolution procedures (Section 2.4). Second, we calculated the RM  
203 compound specific dry deposition velocity using a multi-resistance model<sup>37</sup>. The basic source code of  
204 the multi-resistance model was described in Lyman et al.<sup>33</sup> and was subsequently applied by Huang et  
205 al.<sup>36</sup>. Here the code was modified according to the description in section S6, and is publicly accessible  
206 ([https://github.com/JiaoyanHuang/Dry\\_Depo\\_multi\\_res\\_model](https://github.com/JiaoyanHuang/Dry_Depo_multi_res_model)). The meteorological model input  
207 parameters were derived from hourly ERA5 data, the fifth generation ECMWF atmospheric reanalysis  
208 of the global climate<sup>57</sup>. The meteorological data were representative for a 31 km grid covering the area  
209 around Zeppelin. Snow depth was determined at two measurement stations representing a lower and  
210 upper limit of snow depth in the area. The first station, representing low snow depth, was located on a  
211 measurement field just south of the Ny-Ålesund village; the second station, Bayelva, was located  
212 about 3 km outside the village and represented the upper limit of snow depth<sup>58</sup>. Third, we multiplied  
213 the RM compound specific dry deposition velocities (calculated by the model) with the relative  
214 percentage of the RM compound concentrations measured by the Tekran® or from CEM analysis.

### 215 **2.7 Uncertainty in RM dry deposition modeling**

216 The uncertainty of the modeled RM dry deposition was assessed using the Monte Carlo simulation  
217 approach (Crystal Ball®) and is reported as the 95% confidence interval of 10,000 simulations. The  
218 probability distributions of the key input parameters for the model was obtained using the “BatchFit”  
219 function in Crystal Ball® based on the dataset for each sampling period. Normal distribution and log-  
220 normal distribution were chosen for distribution fitting, and the *p* values for the significance levels of  
221 the fitted distributions were all < 0.05. The uncertainty analysis, however, does not include the issues  
222 of 1) lower sorption efficiency (ca. 50%) of RM on nylon membranes compared to CEMs and 2) that

223 during peak deconvolution mixed compounds, e.g.  $\text{HgBrNO}_3$ , are not well-defined. In order to  
224 minimize these uncertainties, the nylon membranes were not used as a quantitative sorption surface  
225 but for RM compound analysis only. Several studies have confirmed, that nylon membranes sorbed  
226 Hg-Br and Hg-Cl compounds linearly with increasing concentrations (under ambient and laboratory  
227 conditions)<sup>22,53</sup>, and these compounds were neither lost nor transformed RM during sampling and  
228 storage<sup>53</sup>. However, CEM collected systematically higher concentrations of  $\text{HgBr}_2$ ,  $\text{HgCl}_2$ , and a HgO  
229 compound<sup>21</sup>. More recent work has demonstrated that the nylon membranes do not effectively collect  
230 Hg-N compounds<sup>20</sup>. We are learning incrementally about the use of membrane for identifying the  
231 chemistry of the compounds. Thermal desorption and peak deconvolution procedure introduces  
232 uncertainty, because there are only a limited number of RM compounds for which calibration profiles  
233 can be developed and currently the desorption profiles are broad. However, comparing the chemistry  
234 of the compounds to oxidants measured or expected in the air for a variety of locations, as well as ion  
235 chromatography measurement of ions on the nylon membranes, supports the RM chemistry observed.  
236 For example, in Hawaii halogenated compounds were dominant, while in Nevada adjacent to a high  
237 way N-S-O Hg compounds were present, and in a forested area in Maryland organic compounds were  
238 measured<sup>24</sup>. This indicates that we are effectively getting at the compounds in general, although we do  
239 not know the exact chemistry. More work needs to be done to quantify the chemistry and develop  
240 surfaces that are better at retaining compounds.

## 241 **2.8 Auxiliary variables**

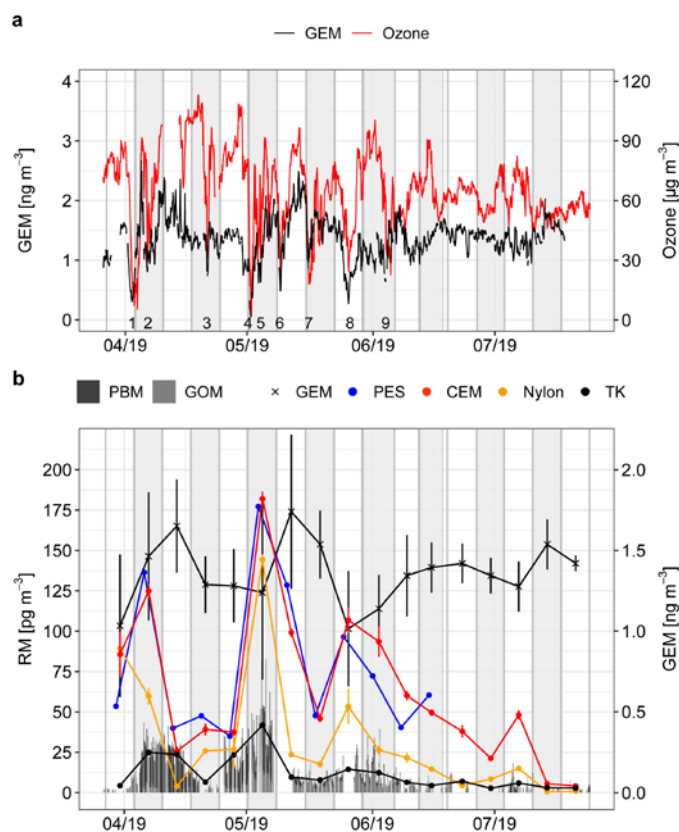
242 Meteorological parameters from Zeppelin, including air temperature, wind speed, wind direction,  
243 relative humidity, and atmospheric pressure, were provided with an hourly resolution by NILU.  
244 Hourly means of tropospheric  $\text{O}_3$  concentrations were measured by NILU using a UV absorption  
245 spectrometer (API 400A). Hourly means of particulate matter concentrations ( $\text{PM}_{2.5}$ ,  $\text{PM}_{10}$ , and  
246  $\text{PM}_{\text{total}}$ ) were derived from a FIDAS® 200S instrument (Palas GmbH, Germany) operated by  
247 Stockholm University (SU). Daily means of particulate and gaseous nitrogen compounds ( $\text{HNO}_3/\text{NO}_3^-$ ,  
248  $\text{NH}_4^+/\text{NH}_3$ ) were collected on a three stage filter pack and analyzed using a Thermo Scientific Dionex  
249 Integriion HPIC System equipped with a Dionex AS9-column<sup>59</sup> and made available by NILU.

## 250 **3. Results and Discussion**

### 251 **3.1 Quantification of atmospheric Hg using the Tekran® system**

252 The mean GEM  $\pm 1\sigma$  concentration measured between March 26 and July 27, 2019 was  $1.36 \pm 0.4$  ng  
253  $\text{m}^{-3}$  (Figure 1a). During that period, nine distinct AMDEs were identified, with eight observed in April  
254 and May and one in early June. The occurrence of an AMDE was defined when GEM decreased below  
255  $1$  ng  $\text{m}^{-3}$ <sup>41</sup> and the  $\text{O}_3$  concentration dropped below the 5<sup>th</sup> percentile ( $33$   $\mu\text{g m}^{-3}$ ). An AMDE starts  
256 when the concentration of GEM sharply decreases and ends when GEM increases again to average  
257 concentrations. Due to AMDEs, GEM concentrations in the Arctic are typically the lowest in April

258 and May. From 2000 – 2009<sup>39</sup> and 2011 – 2015<sup>48</sup>, 86% and 75%, respectively, of annual observed  
 259 AMDEs occurred during the April and May time period. Due to the influence of AMDEs during the  
 260 sampling campaign, the mean GEM concentration during the campaign ( $1.36 \text{ ng m}^{-3}$ ) was lower than  
 261 the annual mean of  $1.54 \pm 0.3 \text{ ng m}^{-3}$  measured between 2000 and 2009<sup>39</sup> and annual means ranging  
 262 from  $1.47 - 1.51 \text{ ng m}^{-3}$  between 2011 and 2015<sup>48</sup>. In summer, GEM increases due to re-emission of  
 263 previously deposited Hg to surfaces and re-emission of surface Arctic Ocean dissolved  $\text{Hg}^0$  <sup>60-62</sup>.



**Figure 1:** Time series of atmospheric Hg species and O<sub>3</sub> from March 26 to July 27, 2019. (a) GEM (black line) and O<sub>3</sub> (red line) concentrations are displayed as hourly means. AMDEs are indicated with numbers 1 to 9. (b) Mean concentration of GEM (black cross), RM on PES (blue dots), RM on CEM (red dots), and RM on nylon membranes (orange dots). RM from Tekran® (TK) measurements (black dots), as PBM and GOM measurements (gray bars), are also displayed. Error bars represent  $1\sigma$  and are indicated where  $n \geq 3$ . PES, CEM, and nylon membranes were deployed for one week. Sampling periods for CEM and nylon membranes are indicated with alternate white and gray backgrounds. The weekly PES sampling was offset from CEM and nylon membrane by one day.

264 Automated Tekran® measurements of RM (GOM+PBM) for the whole sampling campaign were in  
 265 the range of  $2.6 - 13.1 \text{ pg m}^{-3}$  for GOM and  $2.1 - 29.9 \text{ pg m}^{-3}$  for PBM (10<sup>th</sup> and 90<sup>th</sup> percentiles). The  
 266 mean Tekran® RM concentration ( $\text{RM}_{\text{TK}}$ ) was  $14.6 \pm 12.7 \text{ pg m}^{-3}$ , and the values spanned from below  
 267 the MDL to  $82.6 \text{ pg m}^{-3}$  (Figure 1b). During AMDEs, GOM and PBM concentrations were  $9.6$  and  
 268  $20.5 \text{ pg m}^{-3}$ , on average, and elevated by 42% and 54%, respectively, compared to the entire campaign  
 269 average. These values were at the lower end compared to those measured at Zeppelin during AMDEs  
 270 in 2003<sup>41</sup> and in 2007-2008<sup>47</sup>. Overall,  $\text{RM}_{\text{TK}}$  was  $< 43.5 \text{ pg m}^{-3}$  (90<sup>th</sup> percentile) during AMDEs and  
 271 lower ( $< 30.8 \text{ pg m}^{-3}$ , 90<sup>th</sup> percentile) during the entire campaign.

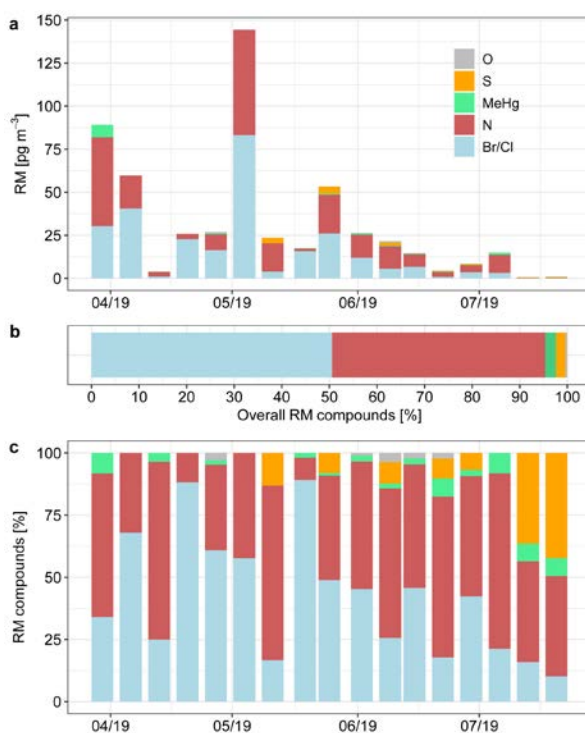
### 272 3.2 Quantification of RM using manual methods

273 Mean RM concentration sampled on CEM ( $RM_{CEM}$ ) was  $63 \pm 45 \text{ pg m}^{-3}$  (Section S3). The highest  
274 concentrations were found between May 1 and May 8 ( $182 \text{ pg m}^{-3}$ ) and lowest at the end of the  
275 campaign from July 17 to July 24 ( $4 \text{ pg m}^{-3}$ ). The large variation among samples was due to the  
276 occurrence of AMDEs until the beginning of June (Figure 1b). Thereafter,  $RM_{CEM}$  tended to decrease,  
277 with one exception from July 3 to July 10 when  $RM_{CEM}$  was  $48 \text{ pg m}^{-3}$ . The RM concentration on PES  
278 ( $RM_{PES}$ ) was sampled until June 18, 2019 and was similar to  $RM_{CEM}$  even though the PES were  
279 replaced one day in advance compared to CEM (slope = 0.91,  $r^2 = 0.86$ ; Figure S1a). The mean  $RM_{PES}$   
280 was  $78 \pm 46 \text{ pg m}^{-3}$ , similar to mean  $RM_{CEM}$  concentrations for the same period to within 2% (March  
281 26 – June 18). The good agreement between the CEM and PES materials was previously demonstrated  
282 by Dunham-Cheatham et al.<sup>53</sup>, showing no significant difference between the two materials ( $\alpha = 0.05$ ).  
283 In concert with that study, the nylon membranes in this study were less efficient at capturing RM.  
284 The mean RM concentration on nylon membranes ( $RM_{Nylon}$ ) was  $32 \pm 37 \text{ pg m}^{-3}$ . The nylon membrane  
285 recovery was 50% (range from 12 to 104%) of the RM sorbed on CEM (Figure 1b). The lower RM  
286 content on nylon membranes was likely due to the different sorption efficiency of varying RM  
287 compounds to this material<sup>19,20,24,36</sup>. Despite the difference in captured RM, the relationship between  
288  $RM_{CEM}$  and  $RM_{Nylon}$  was fairly constant ( $r^2 = 0.75$ ,  $p < 0.05$ , section S3). This supports the conclusions  
289 from previous studies that nylon membranes are not suitable for quantitative RM concentrations, but  
290 are suitable for thermal desorption analysis to identify RM compounds<sup>19,53</sup>.  
291 Weekly mean  $RM_{CEM}$  and  $RM_{PES}$  were up to 19 times and 22 times higher compared to  $RM_{TK}$ ,  
292 respectively (Figure S1b). On average, the  $RM_{CEM}$  was 5.3 times and  $RM_{PES}$  5.2 times higher than  
293  $RM_{TK}$  based on weekly averages ( $11.8 \pm 10.4 \text{ pg m}^{-3}$ ). Tekran® RM measurements were calculated as  
294 the sum of GOM and PBM concentrations and the amount of Hg released during the three 5-min flush  
295 cycles (flush<sub>TK1-3</sub>). The discrepancy between RM on membranes and  $RM_{TK}$  agrees with recently  
296 performed comparisons, where RM on membranes was 2 to 13 times greater<sup>17,18,20-22</sup>. However, we  
297 would like to point out that the impactor on the Tekran® removes particles with aerodynamic  
298 diameters larger than  $2.5 \mu\text{m}$  while the membrane-based systems might also capture particles  $> 2.5$   
299  $\mu\text{m}$ . The mean  $PM_{2.5}$  concentration ( $0.97 \mu\text{g m}^{-3}$ ) was only 30% of the total mean PM concentration  
300 ( $3.29 \mu\text{g m}^{-3}$ ) measured during our campaign. Thus,  $RM_{TK}$  tend to be lower compared to membrane-  
301 based systems due to the lower efficiency of GOM collection<sup>63</sup> and due to the exclusion of large PBM  
302 ( $> 2.5 \mu\text{m}$ ) from analysis. More multi-season  $RM_{CEM}$  and  $RM_{PES}$  timeseries at multiple Arctic sites are  
303 necessary to derive robust correlations with automated measurements and to potentially correct  
304 previous Tekran® RM data.

### 305 3.3 Compounds of RM

306 Thermal desorption and peak deconvolution revealed the composition of RM species that were  
307 retained on the nylon membranes (section S4). The weekly mean  $RM_{Nylon}$  ranged from 1 to  $144 \text{ pg m}^{-3}$

308 (Figure 2a). The dominant RM compounds sampled over the course of the campaign were Hg-Br/Cl  
 309 and Hg-N, that accounted for 51% and 45%, respectively, of the total RM on nylon membranes  
 310 (Figure 2b). Organic-based Hg compounds (e.g. MeHg) contributed 2% to the overall RM  
 311 concentration. Sulfur compounds (Hg-S) accounted also for 2% while the contribution of oxide  
 312 compounds (HgO) was < 1%. The relative contribution of the RM compounds was calculated each  
 313 week throughout the campaign (Figure 2c). The Hg-Br/Cl compounds indicate reactions of GEM with  
 314 halogens (Cl, Cl<sub>2</sub>, Br, Br<sub>2</sub>) within the atmospheric BL<sup>7</sup>, where Br• is regarded as one of the primary  
 315 first-step atmospheric oxidants to produce RM intermediates such as Hg<sup>I</sup>Br<sup>11,64</sup>. The occurrence of  
 316 Hg-N compounds depends on several different factors, such as N emission sources or atmospheric  
 317 redox processes occurring between the source and receptor site<sup>65-67</sup>. Atmospheric NO<sub>2</sub> radicals are also  
 318 considered to be the dominant second-step oxidant transforming Hg<sup>I</sup>Br to Hg<sup>II</sup>BrONO in the free  
 319 troposphere<sup>64,68</sup>. During the first sampling deployment week, RM was composed of 34% Hg-Br/Cl  
 320 and 58% Hg-N compounds, but in contrast, during week two, 68% Hg-Br/Cl and 32% Hg-N were  
 321 detected. During week 6, when two AMDEs occurred and the largest RM concentrations were  
 322 measured (182 pg m<sup>-3</sup>), Hg-Br/Cl and Hg-N contributed similar parts to total RM (58% and 42%,  
 323 respectively). During weeks seven and eight, the dominant RM compound on the nylon membranes  
 324 changed from Hg-N (70%) to Hg-Br/Cl (89%). To explain differences in chemical composition, we  
 325 investigated the role of air mass exposure on the dominant RM compounds, Hg-Br/Cl (51%) and Hg-  
 326 N (45%), along the air mass back trajectory.

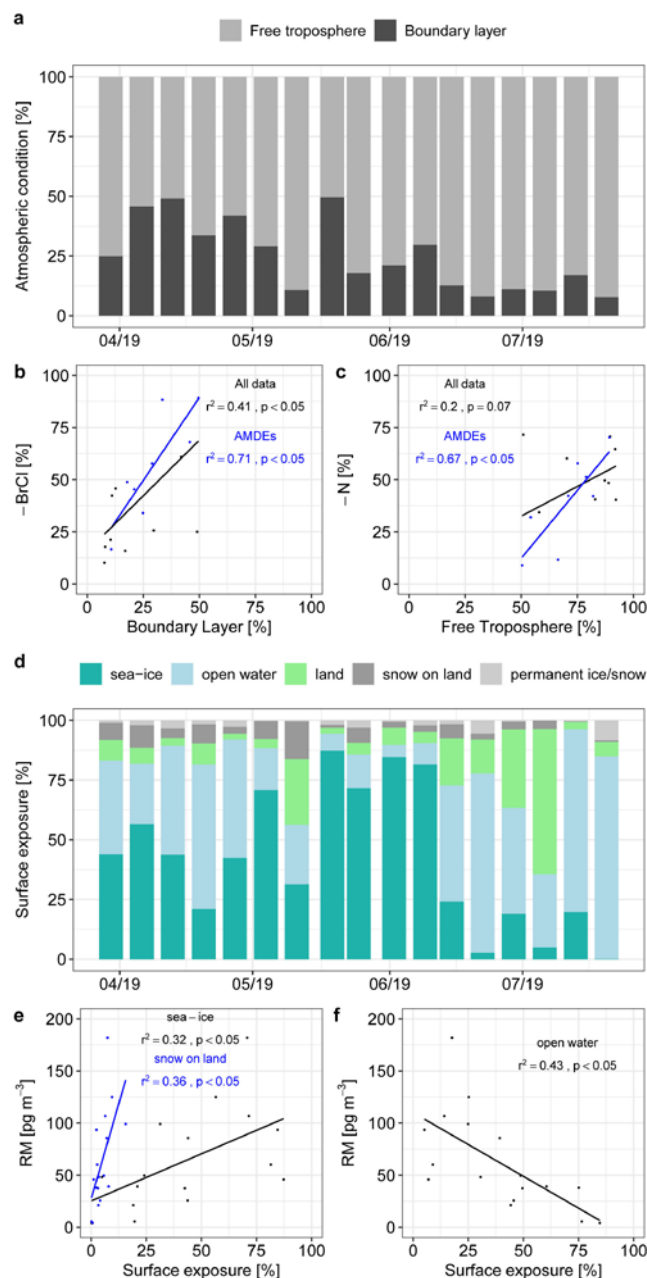


**Figure 2:** RM compounds determined from March 27 until July 24, 2019. (a) The RM concentration on the nylon membrane from the RMAS for a mixture of RM compounds identified by thermal desorption and peak deconvolution. The frequency distribution of RM compounds, in %, is given (b) for the entire campaign (mean) and (c) for each sampling event.

### 327 3.4 Origin of RM

328 To investigate if atmospheric conditions influence the RM compounds, the relationship between the  
329 trajectories within the BL and in the FT was analyzed. The percentage of time the trajectories arriving  
330 at Zeppelin resided in the BL ranged from 7% to 50% (Figure 3a). There was a significant correlation  
331 between the percentage of time the trajectories were within the BL and the determined percentage of  
332 Hg–Br/Cl compounds ( $r^2 = 0.4$ ,  $p < 0.05$ ). The relationship became even stronger during periods when  
333 AMDEs occurred ( $r^2 = 0.7$ ,  $p < 0.05$ ) (Figure 3b). During the same period, Hg–N compounds occurred  
334 more frequently when the advected air mass originated from the FT ( $r^2 = 0.7$ ,  $p < 0.05$ ) (Figure 3c).  
335 This indicates that air masses enriched in Hg–Br/Cl were in contact with the surface for longer periods  
336 compared to air masses enriched in Hg–N, that were originating predominantly in the FT.

337 Air masses arriving at Zeppelin were mainly exposed to sea ice and open water (Figure 3d). The RM  
338 concentrations increased when air masses were exposed to sea ice ( $r^2 = 0.32$ ,  $p < 0.05$ ) or land covered  
339 by snow ( $r^2 = 0.36$ ,  $p < 0.05$ ) (Figure 3e). Lower RM concentrations were measured when air masses  
340 were exposed to open water ( $r^2 = 0.43$ ,  $p < 0.05$ ) (Figure 3f). The positive relationship between Hg–  
341 BrCl and the time the air mass passed over sea ice ( $p = 0.06$ , Figure S4) further corroborates that sea  
342 ice and snow on sea ice are the main source of reactive halogen species in the Arctic that oxidize  
343 GEM. This can occur via one of two mechanisms, activation from snow on sea ice (surface snow  
344 source)<sup>69</sup> or lofted salty snow particles that form sea salt aerosols within the BL (blowing snow  
345 particle source)<sup>70,71</sup>. Though Hg–Br and Hg–Cl compounds are indistinguishable with our methods, all  
346 reactive halogen species in the atmosphere are produced from similar sources, i.e., snow on sea ice and  
347 BL aerosols<sup>72-74</sup>. In the atmosphere, both Br• and Cl• react with O<sub>3</sub> to form halogen oxides<sup>75,76</sup>; both  
348 halogen radicals and halogen oxides lead to the oxidation of GEM to RM<sup>10</sup>.



**Figure 3:** HYSPLIT simulation of air mass trajectory residence time in the atmosphere and exposure to surfaces. (a) Percentage of time the trajectories were in the boundary layer (BL) and free troposphere (FT) for each of the 17 deployment periods. Linear correlation during the entire campaign and during weeks when AMDEs occurred (b) between Hg-Br/Cl and residence time in the BL and (c) Hg-N and residence time in the FT. (d) Surface exposure of trajectories to the 5 major surface categories: sea ice, open water, land (no snow), snow covered land, and permanent ice and snow. Linear correlation between (e)  $RM_{CEM}$  and exposure to sea ice and snow covered land, and between (f)  $RM_{CEM}$  and exposure to open water.

349 A weak positive relationship between Hg-N and the time the air mass passed over land without snow  
 350 cover ( $r^2 = 0.2$ ,  $p = 0.06$ , Figure S4) indicated an anthropogenic source of N compounds (i.e.  $NO_2$ )  
 351 from more densely populated areas further south, or more specifically, springtime transport of plumes  
 352 from Asian industries or Siberian wildfires<sup>77</sup>. Emitted  $NO_2$  leads to enhanced GEM oxidation and  
 353 increased Hg-N concentrations downwind. Though more data are required (multi-seasonal sampling)  
 354 to establish significant relationships between RM compounds and exposure time of air masses to



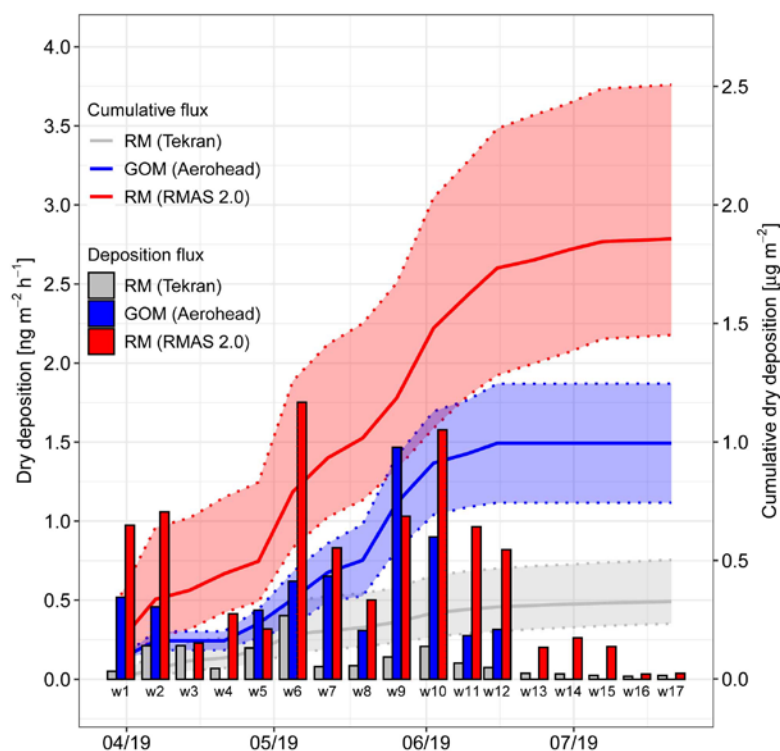
355 different surface types, our conclusions are well illustrated by comparing surface exposure during  
356 weeks seven and eight. A maximum of Hg–N compounds was measured during week 7 (70% of total  
357 RM), when exposure time of air masses over land (43%) and the residence time in the FT (89%) were  
358 long. Back trajectory analysis indicated that the air moved mainly from Fennoscandia (17%) and  
359 Siberia (74%) over the eastern Arctic Ocean to Zeppelin (Figure S5g). The Siberian air mass  
360 originated from areas where wildfires were ubiquitous between May 8 and May 15, 2019  
361 (<https://earthdata.nasa.gov/earth-observation-data/near-real-time/firms>). The mean BL height  
362 measured along the air mass trajectories was 277 m a.s.l and was elevated compared to week 8 (87 m  
363 a.s.l). In week 8, Hg–Br/Cl was the dominant RM compound (89%) and air masses passed  
364 predominantly over sea ice (87%) from areas east of Zemlya Georga and northwest of Svalbard to  
365 Zeppelin (Figure S5h). The residence time of the air mass in the BL was 50%, which corresponded to  
366 the longest residence time in the BL among all weeks of sampling (Figure 3a). Thus, the  
367 comparatively long residence time of air masses within the BL over the sea ice-covered Arctic Ocean  
368 constituted the main source region of Hg–Br/Cl arriving at Zeppelin.

### 369 **3.5 Dry deposition measurements and modeling**

370 Mean local GOM dry deposition at Zeppelin measured by Aerohead samplers was  $0.35 \text{ ng m}^{-2} \text{ h}^{-1}$ , and  
371 weekly averages ranged from below the MDL to  $1.47 \text{ ng m}^{-2} \text{ h}^{-1}$  (Figure 4). Measurements of GOM  
372 dry deposition in 9 out of 17 weeks were above the MDL ( $0.29 \text{ ng m}^{-2} \text{ h}^{-1}$ ). The cumulative Aerohead  
373 GOM dry deposition measured from March 27 to July 24, 2019 was  $1 \mu\text{g m}^{-2}$ , with a 95% confidence  
374 interval ranging from 0.74 to  $1.25 \mu\text{g m}^{-2}$  (Figure 4). Dry deposition of GOM measured by Aerohead  
375 samplers was negligible ( $< 0.1\%$  of the cumulative flux) during the last 5 weeks of measurements  
376 (June 19 to July 27, 2019). During weeks 3 and 4, there was less than 1 pg GOM measured on the  
377 Aerohead CEM, in contrast to 795 pg analyzed on the CEMs from RMAS indicating the importance of  
378 particulate-bound Hg. During weeks 5 and 9, measured GOM dry deposition exceeded the modeled  
379 RM dry deposition by 38% and 43%, respectively. A comparison of meteorological and chemical  
380 variables during these weeks with the preceding and following weeks indicated no unusual conditions.  
381 It could be a compound was present that was sticking to the open-faced membranes in the Aeroheads,  
382 but not making its way into the filter packs holding membranes in the RMAS or the compound had a  
383 higher deposition velocity than other compounds. This would be true for HgO that once formed is  
384 thought to become a particle and rapidly deposit to surfaces<sup>78</sup>. Thus, understanding reactions forming  
385 and the chemistry of compounds of GOM/RM is greatly needed.

386 The cumulative modeled dry deposition of RM, based on RM compound-specific dry deposition  
387 velocities and  $\text{RM}_{\text{TK}}$ , was  $0.33 \mu\text{g m}^{-2}$  with a 95% confidence interval ranging from 0.23 to  $0.50 \mu\text{g m}^{-2}$   
388 (Figure 4). The modeled flux was one-third of the measured flux. The average RM dry deposition  
389 velocities of  $\text{Hg}(\text{OH})_2$ ,  $\text{HgBr}_2/\text{HgCl}_2$ ,  $\text{HgN}_2\text{O}_6$ ,  $\text{HgSO}_4$ , MeHg were very similar and differed by less  
390 than 5% during each sampling week (Table S6). The dominant RM compounds  $\text{HgBr}_2/\text{HgCl}_2$  and

391  $\text{HgN}_2\text{O}_6$  both exhibited a mean deposition velocity of  $0.28 \pm 0.10 \text{ cm s}^{-1}$  over the course of the  
 392 campaign. The weekly mean RM deposition velocities ranged from  $0.12 \text{ cm s}^{-1}$  (week 15) to  $0.48 \text{ cm s}^{-1}$   
 393  $^{-1}$  (week 10). The mean deposition velocity of all RM compounds was  $0.32 \pm 0.09 \text{ cm s}^{-1}$  when the area  
 394 around Zeppelin was covered by snow, and  $0.21 \pm 0.08 \text{ cm s}^{-1}$  during the last five weeks of  
 395 measurements when snowmelt had occurred (June 17, 2019).



**Figure 4:** Measured GOM and modeled RM dry deposition for the entire sampling period. Weekly GOM dry deposition calculated based on the Aerohead system (measured) and RM dry deposition estimated based on the Tekran® and RMAS systems using RM compound-specific dry deposition velocities (modeled). The cumulative flux over the entire sampling campaign (lines) and associated uncertainties (shaded area, 95% confidence interval) are given.

396 The modeled cumulative dry deposition based on  $\text{RM}_{\text{CEM}}$  was  $1.86 \mu\text{g m}^{-2}$  with a 95% confidence  
 397 interval ranging from  $1.45$  to  $2.50 \mu\text{g m}^{-2}$  (Figure 4). Thus, RM dry deposition was 5.6 times larger  
 398 compared to estimates using Tekran® data (Table S7). The discrepancy between the measured  
 399 (Aerohead) and the modeled (RMAS) cumulative dry deposition, a factor of 1.9, was due to the  
 400 Aerohead sampling GOM, while PBM adsorbs negligibly to the down-facing surrogate surface due to  
 401 gravity<sup>22,34-36,79-81</sup>. The inconsistency during weeks 1, 2, and 6 could accordingly be explained by  
 402 elevated concentrations of particulate matter ( $\text{PM}_{\text{total}}$ ), indicating that PBM dominated RM dry  
 403 deposition during these weeks (Figure S2). The inconsistency in weeks 10, 11 and 12, however, was  
 404 likely associated with elevated RM dry deposition velocities ( $0.47 \text{ cm s}^{-1}$ ), given the low PBM  
 405 concentrations, as compared to the other weeks ( $0.25 \text{ cm s}^{-1}$ ) that are not reproduced by the Aerohead  
 406 measurements. It is likely that Hg–N RM compounds were advected on particles, especially during  
 407 weeks 1 and 6 when the absolute amount of Hg–N RM compounds was elevated (Figure 2a). During  
 408 the entire campaign, though, the ammonium ( $\text{NH}_4^+$ ) and nitrate ( $\text{NO}_3^-$ ) aerosol concentration was at  
 409 least three orders of magnitude higher compared to the concentrations of Hg–N compounds. This

410 indicates that RM production and transformation of Hg–N compounds was not directly linked to  
411 advection of particulate nitrogen compounds, which is consistent with a predominant gas-phase  
412 oxidation of RM precursor by NO<sub>2</sub> in the FT<sup>64</sup>.

### 413 **3.6 Implications**

414 Arctic RM concentrations analyzed on CEM and PES were higher than Tekran® RM during all weeks  
415 of measurements. That the Tekran® system significantly underestimated RM concentrations in the  
416 Arctic was surprising since one would expect that most of the RM would be Br and Cl compounds and  
417 given the efficiency of the denuder the KCl denuder it should be 1.2 to 1.3 times lower as  
418 demonstrated in Huang et al.,<sup>21</sup>. But Huang et al.<sup>21</sup>'s experiments were done in clean air whereas the  
419 measurements in the Arctic were of ambient air, indicating the impact of some aspect atmospheric  
420 chemistry (e.g. O<sub>3</sub>) on retention of GOM compounds. The difference between RM concentrations was  
421 large during the AMDE season (mainly April and May) and became small when the RM  
422 concentrations decreased in the summer. In general, RM<sub>TK</sub> showed a significant, but not strong,  
423 correlation ( $r^2 < 0.6$ ) with RM<sub>CEM</sub> and RM<sub>PES</sub>. Bias in denuder-based Tekran® quantification of GOM  
424 could not be corrected, as was suggested for the Pic du Midi high-altitude site in the Pyrenees,  
425 France<sup>25</sup>. The bias in Arctic RM concentration measurements between manual and automated methods  
426 must be addressed not only during AMDEs but with multi-seasonal sampling campaigns at sites such  
427 as Alert in Canada, where Tekran® systems are also operated year-round.

428 RM compound-specific deposition velocity estimates provide the way for more accurate RM dry  
429 deposition estimates. However, as stated in Gustin et al.<sup>63</sup>, the determination of RM compounds could  
430 be improved by: 1) using a new thermal desorption surface, because the nylon membranes  
431 underestimate RM concentrations (by 50% in this study); and 2) identifying the exact chemistry of  
432 RM compounds by developing a mass spectrometry method.

433 The RM dry deposition model revealed higher fluxes when using the RMAS data compared to  
434 Tekran® data, suggesting a 5.6 times larger input of RM to Arctic ecosystems. In the Ny-Ålesund  
435 area, RM dry deposition (1.9 µg m<sup>-2</sup> from March 27 to July 24, 2019) was the dominant Hg deposition  
436 pathway, exceeding mean annual wet deposition ranging from 0.8 to 1.7 µg m<sup>-2</sup> yr<sup>-1</sup> measured between  
437 2012 and 2015<sup>82</sup>.

438 If we accept the assumption that dry deposition measurements made by the Aerohead system are  
439 accurate for GOM and measurements performed with RMAS are accurate for RM, our results  
440 demonstrate that RM bound to particles constituted 46% of the deposited Hg; this also assumes that  
441 RM dry deposition occurs homogeneously and independently of different boundary layer conditions at  
442 Zeppelin. In fact, large particles > PM<sub>2.5</sub> (not analyzed by the Tekran®) contributed 70% to the total  
443 PM concentration (Figure S2). This indicates that a dominant portion of the RM was associated with  
444 large particles (> PM<sub>2.5</sub>), likely marine aerosols. Our study showed that RM dry deposition estimates

445 during the 2019 AMDE season at Zeppelin, and potentially elsewhere in the Arctic, were likely higher  
446 than previously assumed and reported. This has implications for the amount of Hg cycling between the  
447 atmosphere and Arctic ecosystems.

#### 448 **Associated content (Supporting Information)**

449 The Supporting Information (SI) is available free of charge on the ACS publication website. The SI is  
450 structured in six different sections (S1 – S6). We provide details on automated (S1) and manual (S2)  
451 RM sampling and analysis as well as an overview of the measured RM concentrations (S3). The  
452 thermal desorption procedure is described and profiles displayed (S4). Back trajectory modeling is  
453 detailed in S5 and supplementary information about dry deposition modeling is given in S6.

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#### 473 **Data availability**

474 RM concentration data are given in the Supporting Information. A detailed model description is  
475 provided in [https://github.com/JiaoyanHuang/Dry\\_Depo\\_multi\\_res\\_model](https://github.com/JiaoyanHuang/Dry_Depo_multi_res_model). Raw data on thermal  
476 desorption and peak deconvolution procedures or from back trajectory modeling are available on  
477 request.

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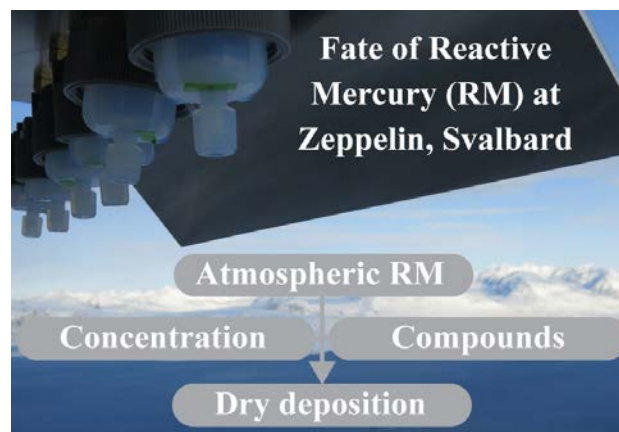
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