



**HAL**  
open science

## Updated Global and Oceanic Mercury Budgets for the United Nations Global Mercury Assessment 2018

P. Outridge, R. Mason, F. Wang, S. Guerrero, Lars-Eric Heimbürger-Boavida

► **To cite this version:**

P. Outridge, R. Mason, F. Wang, S. Guerrero, Lars-Eric Heimbürger-Boavida. Updated Global and Oceanic Mercury Budgets for the United Nations Global Mercury Assessment 2018. *Environmental Science and Technology*, 2018, 52 (20), pp.11466-11477. 10.1021/acs.est.8b01246 . hal-01921166

**HAL Id: hal-01921166**

**<https://hal.science/hal-01921166v1>**

Submitted on 19 Feb 2019

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

## Critical Review

## Updated global and oceanic mercury budgets for the United Nations Global Mercury Assessment 2018

Peter M. Outridge, Robert P. Mason, Feiyue Wang, Saul Guerrero, and Lars-Eric Heimbürger

*Environ. Sci. Technol.*, **Just Accepted Manuscript** • DOI: 10.1021/acs.est.8b01246 • Publication Date (Web): 18 Sep 2018

Downloaded from <http://pubs.acs.org> on September 20, 2018

### Just Accepted

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.

1 **Updated global and oceanic mercury budgets for the United Nations Global Mercury Assessment 2018**

2

3

4 by

5

6 P.M. Outridge<sup>1,2\*</sup>, R.P. Mason<sup>3</sup>, F. Wang<sup>2</sup>, S. Guerrero<sup>4</sup> and L.E. Heimbürger-Boavida<sup>5</sup>

7

8 1: Geological Survey of Canada, Natural Resources Canada, 601 Booth St., Ottawa, ON K1A 0E8, Canada

9 2: Center for Earth Observation Science, Department of Environment and Geography, University of

10 Manitoba, Winnipeg, MB R3T 2N2, Canada

11 3: Department of Marine Sciences, University of Connecticut, 1080 Shennecossett Road, Groton, CT

12 06340, USA

13 4: Universidad Metropolitana, Autopista Caracas Guarenas, Caracas 1073, Venezuela.

14 5: Aix Marseille Université, CNRS/INSU, Université de Toulon, IRD, Mediterranean Institute of

15 Oceanography (MIO) UM 110, 13288, Marseille, France.

16

17

18

19

20 \* Corresponding author email address: [peter.outridge@canada.ca](mailto:peter.outridge@canada.ca) (P.M. Outridge)

**21 Abstract**

22 In support of international efforts to reduce mercury (Hg) exposure in humans and wildlife, this paper  
23 reviews the literature concerning global Hg emissions, cycling and fate, and presents revised global and  
24 oceanic Hg budgets for the 2018 United Nations Global Mercury Assessment. We assessed two  
25 competing scenarios about the impacts of 16<sup>th</sup> - late 19<sup>th</sup> century New World silver (Ag) mining, which  
26 may be the largest human source of atmospheric Hg in history. Consideration of Ag ore geochemistry,  
27 historical documents on Ag production, and comparison of the scenarios against atmospheric Hg  
28 patterns in environmental archives, strongly support a “low mining emission” scenario. Building upon  
29 this scenario and other published work, the revised global budget estimates human activities including  
30 recycled legacy emissions have increased current atmospheric Hg concentrations by about 450% above  
31 natural levels (prevailing before 1450 AD). Current anthropogenic emissions to air are  $2.5 \pm 0.5$  kt/y. The  
32 increase in atmospheric Hg concentrations has driven a ~300% average increase in deposition, and a  
33 230% increase in surface marine waters. Deeper marine waters show increases of only 12–25%. The  
34 overall increase in Hg in surface organic soils (~15%) is small due to the large mass of natural Hg already  
35 present from rock weathering, but this figure varies regionally. Specific research recommendations are  
36 made to reduce uncertainties, particularly through improved understanding of fundamental processes  
37 of the Hg cycle, and continued improvements in emissions inventories from large natural and  
38 anthropogenic sources.

## 39 **Introduction**

40 Mercury (Hg) is released into the environment as a result of human activities, as well as by natural  
41 sources and processes such as volcanoes and rock weathering.<sup>1,2</sup> Following its release, Hg is transported  
42 and recycled among the major environmental compartments – air, soils and waters – until it is  
43 eventually removed from the surface system through burial in coastal and deep ocean sediments, lake  
44 sediments, and subsurface soils.<sup>2,3</sup> However, owing to its long residence times in the oceans and soils,  
45 current concentrations of Hg in the environment are well above those that can be explained by current  
46 releases. Therefore, consideration of historical emissions from natural and anthropogenic sources, and  
47 the on-going recycling of this ‘legacy’ Hg, is an important part of understanding the current global Hg  
48 budget.<sup>4-7</sup> A small fraction on average of the Hg in global aquatic environments is present as  
49 monomethylmercury – the only Hg form that biomagnifies in food chains – although it can be a larger  
50 fraction in some ocean regions and specific water masses.<sup>2</sup> For the sake of simplicity,  
51 monomethylmercury is referred to by its generic name, methylmercury (MeHg). Many of the processes  
52 involved in Hg methylation, or influencing MeHg uptake into food chains, are still inadequately  
53 understood<sup>8,9</sup>, which contributes to the difficulties in precisely predicting the effects of regulatory  
54 action on wildlife and human Hg exposure.

55 To address the global problem of Hg pollution, the Minamata Convention was adopted by the United  
56 Nations in 2013 ([www.mercuryconvention.org](http://www.mercuryconvention.org)) and entered into force in August 2017. As part of efforts  
57 to support the Convention, the United Nations Environment Programme (UNEP) is undertaking regular  
58 assessments of the scientific literature on Hg at five-year intervals. An improved quantitative  
59 understanding of the global Hg cycle is important for our capacity to predict how regulatory actions to  
60 reduce emissions will affect Hg concentrations in different environmental compartments, biota and  
61 humans. Given its scale and biogeochemical complexity, and the lack of detailed information for many  
62 of its aspects, the planetary Hg cycle is best described using budgets derived from global-scale models

63 and literature compilations. This review presents a synthesis of recent advances since the AMAP/UNEP  
64 report<sup>1</sup> in our understanding of the global Hg cycle, including an evaluation of the influence of historical  
65 emissions on current anthropogenic Hg levels in the biosphere, and provides updated global and oceanic  
66 total Hg budgets that are incorporated into the 2018 Global Mercury Assessment.<sup>10</sup>

### 67 **A General Overview of Recent Advances**

68 In the technical background report to the 2013 Global Mercury Assessment<sup>1</sup>, based on a global budget  
69 developed by Mason et al.<sup>11</sup>, it was estimated that human activities had increased atmospheric Hg  
70 concentrations by 300–500% since about the end of the 19<sup>th</sup> century. Mercury concentrations in surface  
71 ocean waters less than 200 m deep had increased on average by ~200% over the past century, whereas  
72 deeper waters exhibited smaller increases (11–25%) because of the century- to millennium-scale  
73 residence times of these slowly overturning water masses. The average Hg increase in surface organic  
74 soils was estimated at ~20% and was negligible in mineral soils.

75 Recent studies<sup>4, 7, 12, 13</sup> have emphasized the point that the end of the 19<sup>th</sup> century, or even the last few  
76 centuries of the so-called “pre-industrial period”, are not a suitable natural or “pre-anthropogenic”  
77 reference point from which to gauge the full impact of human activities on the current global Hg cycle.  
78 Studies of Hg consumption and production during New World precious metal and cinnabar (Hg ore)  
79 mining from the 16<sup>th</sup> century onwards<sup>14, 15</sup>, and re-examination of the atmospheric Hg fluxes recorded in  
80 long lake sediment and peat cores covering most of the last millennium<sup>7</sup>, indicate that significant  
81 amounts of Hg were emitted by human activities in the period after the 16<sup>th</sup> century, and before the  
82 mid-19<sup>th</sup> century when the “pre-industrial period” is often regarded as having ended (e.g.,<sup>16, 17</sup>). There  
83 are different definitions of a time that represents truly natural or ‘pre-anthropogenic’ conditions: e.g.,  
84 2000 BC<sup>13</sup>, 3000 BC to 1550 AD<sup>7</sup>, or prior to 1450 AD.<sup>18</sup> For the purposes of this review we adopted  
85 Zhang et al.’s<sup>5</sup> definition of 1450 AD as the end of the pre-anthropogenic era.

86 As with almost all global trace metal budgets, uncertainties exist regarding the amounts of  
87 anthropogenic and natural Hg 'stored' in different environmental compartments, the fluxes between  
88 them, and the rates of removal of Hg from the biosphere.<sup>1</sup> Major ongoing efforts have been mounted to  
89 reduce these uncertainties. Since 2011, additional measurements of Hg concentrations and fluxes in  
90 oceans, atmosphere and soils have led to suggested refinements of global budgets and models<sup>4-7, 12, 13,</sup>  
91<sup>18-20</sup>. Major uncertainties persist, however, especially in estimates of the amount of anthropogenic Hg in  
92 the oceans (cf.<sup>5, 13</sup>).

93 Despite differences in definition of the "natural" period in Hg contamination history, the two most  
94 comprehensive, recent global Hg budgets generally agree that human activities have increased  
95 atmospheric Hg concentrations by a similar range: 450%<sup>5</sup> to 660%<sup>13</sup>, such that total atmospheric  
96 concentrations today are 5.5-fold to 7.6-fold higher than natural levels, respectively. These estimates  
97 include revolatilized legacy Hg. There are greater differences in the budgets' estimates of atmospheric  
98 Hg deposition increases. Zhang et al.<sup>5</sup> calculated that there had been an average 4.8-fold increase in  
99 deposition to oceans and a 7.8-fold increase to land. However, Amos et al.<sup>13</sup>, by modeling various  
100 emission scenarios and comparing these trends with a re-evaluation of long peat and lake sediment  
101 cores, and the Hg concentration in surface reservoirs, proposed substantially higher increases. Median  
102 increases in Hg accumulation rates between the pre-anthropogenic period and the 20th century peak  
103 were a factor of ~26 in peat bogs and ~14 in lake sediments, with both archive types showing increases  
104 of about 5-fold between the pre-anthropogenic and the pre-industrial (i.e., 1760-1880) periods. By  
105 analysing Hg isotopes in Pyrenean peat cores, Enrico et al.<sup>21</sup> reported that maximum 20<sup>th</sup> century  
106 concentrations of gaseous elemental Hg (Hg(0); GEM) were 15±4 times higher than in the early- to mid-  
107 Holocene. These increases are several times higher than other, sediment-based literature had indicated,  
108 of a ~3-fold increase due to anthropogenic activities.<sup>2, 16, 22</sup> Amos et al.<sup>7</sup> attributed the lower estimates to  
109 an erroneous selection of natural deposition values that were too high, because they were based on 18<sup>th</sup>

110 and early 19<sup>th</sup> century sediment samples that were already contaminated with mining-emitted Hg. Thus,  
111 studies since about 2012 indicate that the true impact of anthropogenic emissions on atmospheric Hg  
112 deposition, based on a comparison to pre-anthropogenic values, is greater than previous comparisons to  
113 the 19<sup>th</sup> century had suggested. But there is considerable variation in the estimates of the degree of that  
114 impact.

115 The differences between the two most recent global budgets<sup>5, 13</sup> are most apparent in their estimates of  
116 the amount of anthropogenic Hg in today's oceans. The primary cause is their varying estimates of the  
117 amount and environmental fate of atmospheric emissions from historical silver (Ag), cinnabar (Hg) and  
118 gold (Au) mining in the Americas between the 16<sup>th</sup> and late 19<sup>th</sup> centuries, and to differences in the  
119 estimated amount of natural Hg originally present in the oceans. Both studies based their global budget  
120 calculations on Streets et al.'s<sup>4</sup> all-time emission inventory, with Zhang et al.<sup>5</sup> reducing the emissions  
121 from Ag mining by three-fold. For convenience, we will refer to these two emissions scenarios as "low  
122 mining emissions" and "high mining emissions", represented by Zhang et al.<sup>5</sup> and Amos et al.,<sup>13</sup>  
123 respectively, although each of these papers is underpinned by a wealth of supporting literature  
124 published before and since their respective publication. Overall, the chemical rate constants used for  
125 modelling circulation processes within and between oceanic, atmospheric and terrestrial compartments  
126 are a secondary factor differentiating the two scenarios.

127 Considerable Hg releases to land, freshwaters and air are known to have occurred from the mining and  
128 production of Ag (as well as Hg and Au) in South/Central America during the Spanish colonial period  
129 (about 1520–1850 AD), and later from North American artisanal and small-scale mining during the "Gold  
130 Rush" era (roughly 1850–1920).<sup>15, 23-25</sup> It is generally agreed that some fraction of the Hg from both  
131 historical periods is still circulating within the global biosphere, and that this has had an effect on  
132 present-day environmental Hg levels. But quantification of that effect is uncertain. Thus, before revising



133 the global and oceanic budgets, evidence for the impact of historic mining on the global environment  
134 and its relative importance in the different scenarios must be evaluated.

### 135 **Influence of Historic Ag Mining on Anthropogenic Hg Emission Inventories**

136 The total amount of Hg currently in the environment reflects a mixture of sources: historical  
137 anthropogenic releases to air, land and waters; historical natural inputs; and present-day anthropogenic  
138 and natural releases. Streets et al.'s<sup>12</sup> updated inventory of all-time Hg emissions concluded that  
139 historic Ag mining and production was the largest single source of anthropogenic Hg to the  
140 environment, contributing several-times more Hg to the atmosphere (146 kt, 31% of total emissions)  
141 than combined industrial and artisanal Au production (55.4 kt) or coal combustion (26.4 kt). Mercury  
142 production, much of which was destined for use with small-scale Ag and Au mining, contributed the  
143 second highest amount, 91.7 kt. Most of the Ag mining-related Hg releases to air occurred before 1920.

144 A historical analysis of elemental Hg importation and consumption in the 16<sup>th</sup> to 19<sup>th</sup> centuries, in what  
145 is today Mexico, Peru and Bolivia, indicated that large quantities of liquid Hg were indeed used during  
146 Spanish colonial Ag production.<sup>14</sup> Mercury was also refined from cinnabar at two major sites in the  
147 Spanish New World, as well as in California, and at Idrija and Almaden in Europe.<sup>15</sup> During the 250 years  
148 after ~1560, records indicate that over 120 kt of liquid Hg (average of at least 0.48 kt/y) was imported  
149 from Europe into the New World or produced in the region, and virtually all of this was lost to the  
150 regional environment.<sup>26</sup> Given the likely large scale of contraband Hg involved in mining, this amount  
151 may be considerably underestimated. Because of the importance of legacy Hg in the modern  
152 environment, a correct interpretation of the impact of historic Ag mining emissions on the current  
153 global Hg budget is particularly critical.<sup>5,7,27</sup>

154 Streets et al.'s<sup>4,12</sup> inventories assumed emission factors of 52% and 40%, respectively, to calculate  
155 atmospheric Hg emissions from historic Ag mining, based on Ag metal production data. These factors

156 represent the putative fraction of the Hg utilized in Hg mining that was ultimately emitted to the  
157 atmosphere, and were adapted from Nriagu's estimates<sup>23, 24</sup> based on artisanal Au mining. This form of  
158 small-scale Au mining commonly used direct amalgamation of Au with elemental Hg (a physical  
159 process), which was then heated to recover the Au. In contrast, the nature of Ag ore geochemistry, and  
160 different Ag production practices, meant atmospheric Hg emissions were much lower per unit of historic  
161 Ag metal production than from artisanal Au.<sup>14, 15, 27</sup> Unlike Au, the Ag in economic ores mostly does not  
162 occur in its elemental form. Smelting (without any Hg involvement) was applied to Ag-rich galena (PbS)  
163 or copper ores, producing about half of all global Ag production up to 1900.<sup>27, 28</sup> Thus, Hg emissions from  
164 this industry must have come only from the non-smelted half, using other ore types. Many other Ag-  
165 rich ore bodies, including those in the New World, are predominantly silver sulfide (acanthite, Ag<sub>2</sub>S) with  
166 silver chloride in varying proportions.<sup>15, 29</sup> Historic refining of these ores used Hg, and involved two  
167 distinct but concurrent chemical reactions: an oxidative chloride leach to convert silver sulfide to silver  
168 chloride, and a redox reaction with Hg to produce metallic silver from silver chloride, followed by  
169 amalgamation of the Ag with excess Hg.<sup>30</sup> The AgHg amalgam was then heated to remove the Hg. These  
170 Spanish colonial practices were later employed during the 19<sup>th</sup> century North American Gold Rush,  
171 except that iron was added to the chemical slurry to reduce Hg loss to insoluble calomel (Hg<sub>2</sub>Cl<sub>2</sub>).<sup>27</sup> In  
172 the refining process, the major cause of Hg loss was calomel formation, with minimal volatile emissions  
173 even during the heating stage.<sup>27, 30</sup> Mercury was carefully controlled during these reactions and during  
174 heating, and was recycled as much as possible because Hg was expensive relative to Ag, unlike the  
175 current situation where Hg is cheap relative to Au. The calomel reaction in the Hg treatment of Ag ores  
176 has been confirmed by laboratory experiments.<sup>31</sup> The waste rock tailings were typically disposed of with  
177 the calomel, thereby burying it in soils and sediments, although its long-term fate in the environment  
178 has not yet been studied.

179 In contrast to the use of emission factors with Ag production data to estimate Hg releases, Guerrero<sup>14</sup>  
180 used importation statistics and consumption records on Hg itself, from Spanish colonial government and  
181 independent observers. His calculations suggested that no more than 7–34% of the Hg used during Ag  
182 production was physically lost through volatilization, ground spills and in waste water, with 66–93% of  
183 the consumed Hg chemically transformed into calomel. Volatilization was thus a small fraction (<34%) of  
184 total Hg consumption. During the 19<sup>th</sup> century, numerous sources reported Hg losses to air of less than  
185 1% of the Hg consumed by refining<sup>15, 27, 30</sup>, owing to improvements in the equipment used to recapture  
186 and condense gaseous Hg after amalgamation and heating. Thus, the putative 40-52% emission factors  
187 for Ag mining appear to be inconsistent with newly available historical and chemical information.  
188 Recognition of the importance of history and chemistry in resolving the role of Ag mining is an important  
189 recent advance, and represents a fundamental difference between the low and high mining emission  
190 scenarios discussed in this review.

191 The AMAP/UNEP report<sup>1</sup> used an emission factor of 45% for Hg emissions from artisanal and small-scale  
192 gold mining (ASGM) in the present-day. That estimate is not affected by the new evidence concerning  
193 Ag mining. The Au amalgamation process with Hg does not involve calomel formation, and thus historic  
194 Hg losses from Ag mining are not representative of those from ASGM<sup>30</sup>, which are likely to be higher as  
195 there is little attempt to recover Hg during heating of the amalgam.

### 196 **Evidence from Natural Archives**

197 Based on Guerrero<sup>14</sup>, Zhang et al.<sup>5</sup> adopted a low emission factor of 17% for Hg from Spanish colonial  
198 and 19<sup>th</sup> century Gold Rush Ag mining. The resulting all-time cumulative anthropogenic emissions to air  
199 (190 kt<sup>5</sup>) were just over half those estimated by Streets et al.<sup>4</sup> of 351 kt), with decidedly lower releases  
200 during the Spanish colonial and Gold Rush periods (Fig. S1a). Modeling of Hg deposition based on the  
201 low emission scenario predicted fluxes markedly closer to measured values in 120 widely dispersed lake

202 sediments around the world, compared to those based on another model with the high emission  
203 scenario (see Fig. S1b, c, d). A more recent estimate for all-time anthropogenic releases to air at 472 kt<sup>12</sup>  
204 was even higher than Streets et al.,<sup>4</sup> because of added commercial product emissions after the late  
205 19<sup>th</sup> century<sup>6</sup>, but this addition would not affect the high emission scenario prediction concerning  
206 historical Ag mining.

207 Support for the low emission scenario came from an independent analysis by Engstrom et al.<sup>22</sup> of  
208 another large global set of lake sediment Hg profiles independent from those in Zhang et al.<sup>5</sup>. Although  
209 atmospheric Hg deposition was substantially increased during the Spanish colonial period in one South  
210 American lake (Laguna Negrilla) near the major cinnabar mining and Hg production site of Huancavelica,  
211 Peru, there was little evidence of increased deposition at this time in sediment cores from many remote  
212 North American, Arctic or African lakes, suggesting that the contamination from Ag-, Hg- and Au-mining  
213 was, at most, limited to surrounding terrestrial, freshwater and coastal ecosystems in western  
214 South/Central America.<sup>22</sup>

215 Similarly, there is little evidence in natural archives to support a major atmospheric Hg impact from late  
216 19<sup>th</sup> century North American Gold Rush mining. Streets et al.'s<sup>4</sup> results suggested a bimodal pattern of  
217 total anthropogenic Hg emissions to air and modeled atmospheric concentrations from 1850 onwards,  
218 with values in the 1890s that were as high or higher than in the mid- to late 20<sup>th</sup> century, due to a 450%  
219 increase in primary emissions mostly from Gold Rush Ag mining. A revision to include Hg releases from  
220 commercial products from the late 1800s onwards<sup>6</sup> did not substantially diminish the late 19<sup>th</sup> century  
221 peak in emissions and atmospheric concentrations (see<sup>12</sup>). Although increases in Hg accumulation  
222 occurred in remote lake sediments at this time, they were small relative to those observed later in the  
223 20<sup>th</sup> century in the same core profiles.<sup>5, 22, 25</sup> Thus, the world-wide lake sediment record appears to  
224 suggest a negligible global impact from Ag, Hg and Au production during the 16<sup>th</sup> to early 20<sup>th</sup> centuries.  
225 Coincident increases in atmospheric emissions from other sources such as coal combustion and

226 commercial Hg uses<sup>12, 32</sup> may have contributed to the steady increase of Hg in world-wide deposition  
227 (see above) and in Arctic marine biota<sup>33</sup> that started in the latter half of the 19<sup>th</sup> century.

228 Amos et al.<sup>7</sup> discounted the lake sediment evidence by arguing that sediments in general respond  
229 relatively slowly and insensitively to changes in atmospheric Hg deposition compared with peat bogs.

230 Amos et al.<sup>7</sup> also proposed that the Guerrero<sup>14</sup> volatilization estimate was unrealistically low because it  
231 omitted Hg losses during reprocessing of Hg-containing Ag and Au products, and revolatilization from  
232 solid mining wastes including calomel. There is some evidence that calomel may disproportionate to  
233 Hg(0) and Hg(II) under ambient environmental temperatures and sunlight<sup>34</sup>, but the extent of such  
234 disproportionation has not yet been studied under realistic controlled conditions. Evaluation of  
235 alternative global model scenarios by Amos et al.<sup>7</sup> suggested that the low emission scenario was  
236 inconsistent with Hg measurements in present-day environmental matrices, as well as with the  
237 magnitude of Hg enrichment in peat and some lake sediment archives. However, examination of the  
238 published outputs in Amos et al.<sup>7</sup> showed that the “mining reduced 3x” scenario actually gave better  
239 agreement with observed upper ocean total Hg concentrations and net oceanic evasion rates than the  
240 high emission scenario based on Streets et al.<sup>4</sup>, with similar estimates for present-day soil Hg  
241 concentrations and net terrestrial flux (see Figs. 3d, 3g, 3f and 3h, respectively, in ref. 7). Furthermore,  
242 the lake sediment-based interpretations (above) of Strode et al.<sup>25</sup>, Engstrom et al.<sup>22</sup> and Zhang et al.<sup>5</sup>  
243 were supported by peat bog studies from the Faroe Islands<sup>35</sup>, Maine, USA<sup>36</sup>, Swiss Jura Mountains<sup>37</sup> and  
244 the Pyrenees<sup>21</sup> that all showed relatively muted Hg increases prior to 1900, and with 20<sup>th</sup> century  
245 accumulation rates substantially higher than in the late 19<sup>th</sup> century. Recently published high-resolution  
246 marine sediment cores from a remote region in the Southern Ocean<sup>38</sup>, and off New England, USA<sup>39</sup>,  
247 also provide no evidence of significant global dispersion of emissions from historic Ag, Hg and Au  
248 mining.

249 Additional independent evidence supporting the low emission scenario, and the sediment and peat bog  
250 patterns, was provided by recent studies of glacier ice cores (Fig. 1). In contrast to the modeled 450%  
251 increase in global primary Hg emissions between 1850 and 1890<sup>12</sup>, three ice cores displayed increases in  
252 Hg accumulation between 1840-60 and 1880-1900 of 40 to 150% (reanalysis of data from refs. <sup>40-42</sup>). All  
253 three studies indicated that Hg accumulation rates were substantially greater after 1950 than in the late  
254 1800s, in contrast to the high emission scenario prediction (see Fig. S1). Furthermore, in a core from  
255 Mount Logan, Yukon, the peak periods of Spanish colonial mining (~1600–1850) and the North American  
256 Gold Rush (1850–1900) represented only 8% and 14%, respectively, of total anthropogenic Hg  
257 deposition in the core, with 78% occurring during the 20<sup>th</sup> century.<sup>40</sup> Finally, it should be noted that the  
258 Freemont Glacier ice core, that has been cited as evidence to support significant emissions from the  
259 North American Gold Rush, has had its chronology revised. With this new dating, the Hg profile is now in  
260 good agreement with the other ice core studies, and shows little evidence for Hg emissions during the  
261 Gold Rush.<sup>43</sup>

262 Thus, the weight of natural archive evidence, as well as new historical and chemical information (above),  
263 supports the low mining emission scenario, and suggests that any atmospheric Hg emissions produced  
264 by historical Ag, Au and Hg production were restricted to areas around some mining operations. Other  
265 studies have shown marked local contamination by nearby historic Ag, cinnabar and Au mining<sup>17,44</sup>,  
266 although these effects are not seen everywhere (e.g. <sup>43</sup>).

### 267 **Revised Global and Oceanic Total Hg Budgets**

268 Here we present the updated budgets included in the 2018 AMAP/UNEP report<sup>10</sup>, explain how they  
269 were developed, and specify how the two main contrasting views of the world's historical emissions<sup>5,7,13</sup>  
270 compare with each other in terms of the current budget. In general, the revised global Hg budget (Fig. 2)  
271 was constructed by updating the previous version<sup>1,11</sup> with results from Zhang et al.'s model<sup>5</sup> and after

272 consideration of much of the new information and mass and flux estimates published by different  
273 groups since 2012 (see Table S1, Supplementary Material).

274 Estimates of the amounts of natural and anthropogenic Hg in the atmosphere by Amos et al.<sup>13</sup> and  
275 Zhang et al.<sup>5</sup> agreed to within about 30% of the estimates in the AMAP/UNEP budget<sup>1</sup> (Table 1). We  
276 accepted Zhang et al.'s<sup>5</sup> estimate that human activities have increased current atmospheric Hg  
277 concentrations by about 450% above natural levels (defined as those prevailing before 1450 AD). This  
278 represents an increase of 3.6 kt in atmospheric Hg mass above the natural value of 0.8 kt, for a total of  
279 4.4 kt. We calculated that the increase in atmospheric Hg concentrations has driven a ~300% average  
280 increase in deposition, which is the largest source of Hg (~90%) entering the surface ocean.<sup>11</sup> Surface  
281 marine waters have shown an average 230% increase in Hg concentrations above natural levels,  
282 showing some lag with atmospheric changes given the longer residence time of Hg in surface waters.  
283 Deeper marine waters in our budget show increases of only 12–25% owing to the slow rate of  
284 penetration of anthropogenic Hg into the large deep-water reservoir, which is again consistent with the  
285 literature<sup>18-20</sup>, and estimates of deep ocean Hg sediment accumulation. However, our estimate for  
286 ocean accumulation (see Fig. 3), while consistent with prior literature and modeling, is lower than and  
287 not consistent with Zaferani et al.'s<sup>38</sup> recent Holocene-long marine sediment core study from remote  
288 Antarctica, in a region of high sediment accumulation. More research is clearly needed to further  
289 constrain the magnitude of deep ocean net burial. The overall increase in Hg in surface organic soils  
290 (~15%) is small due to the large mass of natural Hg already present from rock weathering, but this  
291 figure varies regionally because of variations in natural features and processes such as vegetation cover  
292 and soil organic matter, as well as anthropogenic inputs.<sup>45</sup>

293 The new terrestrial reservoir and flux estimates (see Table 1 and Fig. 2) were updated from Driscoll et  
294 al.<sup>19</sup> and Amos et al.<sup>7</sup> Specific fluxes were also adopted from Pacyna et al.<sup>46</sup> and Cohen et al.<sup>47</sup>, who  
295 advocated for particular values from biomass burning, soil and vegetation emissions, and geogenic

296 sources. The revised soil plus vegetation emissions are lower than the AMAP/UNEP<sup>1</sup> value, but for most  
297 of the remaining fluxes, the changes are relatively small (<30%) compared to the previous estimates.  
298 Both Amos et al.<sup>13</sup> and Zhang et al.<sup>5</sup> suggested that soils globally contain more anthropogenic Hg than  
299 was stated in AMAP/UNEP<sup>1</sup>, and these more recent values were considered in our reanalysis. The  
300 relative anthropogenic:natural balance in riverine fluxes in Figs. 2 and 3 was revised considering the  
301 estimates of Zhang et al.<sup>5</sup>, Liu et al.<sup>48</sup>, and Kocman et al.<sup>49</sup>

302 Fluxes between the atmosphere and terrestrial and oceanic reservoirs were modified in accordance with  
303 our best estimate for global atmospheric anthropogenic emissions (2.5 kt/yr), which is 25% higher than  
304 in AMAP/UNEP,<sup>1</sup> and using the relative anthropogenic:natural flux estimates from Zhang et al.<sup>5</sup> The  
305 higher emissions value reflects the fact that the documented emission inventory presented in the 2018  
306 Global Mercury Assessment (2.15 kt/yr for 2015<sup>10</sup>) acknowledges that emissions for several sectors  
307 cannot be reliably quantified and so are omitted. Provisionally, these sectors, which include agricultural  
308 waste burning and municipal and industrial waste disposal, can be expected to contribute tens to  
309 hundreds of additional tonnes of atmospheric Hg. The 2.5 kt/yr value adopted here is therefore  
310 considered to be a conservative estimate for use in a contemporary global budget calculation. This  
311 estimate contains several acknowledged uncertainties (especially for emissions from ASGM, and waste  
312 combustion) and so a relatively wide uncertainty of  $\pm 0.5$  kt/yr is included. Similarly, there is a large range  
313 in estimates for ocean evasion, and the value adopted here represents the lower evasion estimates from  
314 recent high-resolution measurements (e.g.,<sup>50</sup>). A new estimate for total anthropogenic releases from  
315 point sources to freshwaters, of 0.6 kt/yr<sup>10</sup>, is included based on recent literature.<sup>7,49</sup> An estimate for oil  
316 and gas releases to marine systems (0.015 kt/yr<sup>10</sup>) was insignificant compared with the other fluxes and  
317 so is not included in Fig. 2. No reliable estimates of natural terrestrial Hg fluxes to freshwaters at a global  
318 scale were available, and thus this pathway was not quantified. Riverine fluxes into the open ocean are  
319 reduced by particule scavenging and sedimentation in estuaries and coastal seas, and the estimate used



320 here is the lowest of those in recent models (<sup>3,5,7</sup>). Kocman et al.'s <sup>49</sup> compilation and evaluation of  
321 global freshwater Hg contamination suggested that Liu et al.'s <sup>48</sup> measurements of Chinese riverine Hg  
322 fluxes were consistent with their data, and were more reliable and significantly lower than Amos et al.'s  
323 (2014) modeling study. Kocman et al. <sup>49</sup> advocated for a relatively low global riverine flux value similar to  
324 that of Sunderland and Mason <sup>51</sup>. The anthropogenic fraction in the freshwater flux entering oceans is  
325 increased by upstream urban/industrial point sources so that the anthropogenic:natural ratio is higher  
326 than the small anthropogenic fraction in organic soils (~15%) would suggest. Overall, flux uncertainties  
327 in the budget should each be regarded as spanning a range of at least  $\pm 20\%$ , and subject to future  
328 revision. The mass budget is balanced to within 5%.

329 A recent paper by Schuster et al. <sup>52</sup> suggested that melting of permafrost in the Arctic could be a globally  
330 significant additional source of soil Hg to the atmosphere and aquatic systems in future. A major reason  
331 for discrepancies between that paper and other estimates of the soil Hg reservoir is the depth of Hg  
332 concentration data integration. Mason et al. <sup>53</sup> and most subsequent modeling and budget estimates  
333 reported the amount of Hg in a surface active soil layer of a certain thickness (e.g. 10 cm) or reflected a  
334 specific soil pool (e.g., the fast recycling pool in many models; ~4% of the total soil reservoir). Schuster  
335 et al. <sup>52</sup> integrated to a depth of several meters, but then compared their values to the previous  
336 estimates for surface pools. Such comparisons can lead to incorrect conclusions, and so for the soil  
337 reservoir the integration depth is a critical parameter. Here we use the amount of Hg in the actively  
338 recycling soil pool (i.e., with an average depth of 10 cm).

339 With respect to the world's oceans, there are significant differences between recent papers concerning  
340 the quantity of anthropogenic Hg presently circulating in seawater. <sup>5,7,13,20</sup> Up to 2012, published  
341 estimates of the oceanic anthropogenic Hg mass ranged over more than an order of magnitude, from  
342 7.2 to 263 kt. <sup>4,11,51,53-57</sup> Since then, Amos et al. <sup>13</sup> derived another estimate (222 kt) near the upper end  
343 of this range based on the historical mining-influenced high emission scenario. As described above,

344 additional evidence published since 2012, and considerations of Ag ore geochemistry and production  
345 techniques, strongly support Zhang et al.'s<sup>5</sup> suggestion that the high emissions scenario is too high.

346 Even with the lower mining emissions scenario, Zhang et al.'s<sup>5</sup> calculations indicated that the  
347 cumulative impact of those emissions over four centuries has been substantial, with 67% of the increase  
348 in oceanic Hg mass above natural levels occurring prior to 1920, and mostly ascribed to Ag mining-  
349 related airborne contamination. The total anthropogenic mass in today's oceans (66 kt) estimated by  
350 Zhang et al.<sup>5</sup> is in good agreement with another recent estimate ( $58 \pm 16$  kt<sup>20</sup>) derived using a different  
351 methodology based on seawater Hg concentration profiles combined with anthropogenic CO<sub>2</sub> and  
352 remineralized phosphate as proxies for oceanic Hg distribution. That the two studies, using different  
353 approaches, arrived at similar estimates increases confidence in the robustness of their conclusions.  
354 Both recent estimates fall within the lower half of the previous range of values and are close to the  
355 Mason et al.<sup>11</sup> estimate of 53 kt used in AMAP/UNEP<sup>1</sup> (see Table 1).

356 Based on this revised global budget, the Hg budget in the world's oceans, as represented in Zhang et al.<sup>5</sup>  
357 was updated in light of the mass balance fluxes and reservoirs in Fig. 2, and is presented in greater detail  
358 in Fig. 3. The ratios of natural to anthropogenic Hg reported by Zhang et al.<sup>5</sup> were retained for most of  
359 the reservoirs and fluxes, although their relative increase in oceanic Hg mass due to anthropogenic  
360 inputs is higher than in other publications. This difference was taken into account in updating and  
361 revising their budget for this paper. In Figure 3, each reservoir and flux term includes both the natural  
362 and anthropogenic contribution. The graphic also shows the cycling of Hg in the ocean through  
363 scavenging by particulate organic matter, which is a major mechanism for transport of Hg between  
364 surface waters and deep ocean (e.g., see<sup>38</sup>). In this graphic, the intermediate and deep waters are  
365 combined, whereas they are treated separately in the global budget in Fig. 2.

366 In addition to differences in the amount of anthropogenic Hg in the world's oceans, the balance of  
367 anthropogenic Hg distribution between global soils and oceans differs between budgets, with oceans  
368 holding either about as much anthropogenic Hg mass as the actively recycling soils<sup>1,5</sup> or substantially  
369 less.<sup>13</sup> The difference between outcomes may be partly due to our lack of understanding of some of the  
370 basic processes governing Hg transport and fate in the terrestrial environment. For example, recent  
371 studies on atmospheric Hg dynamics under a range of different plant communities – from tundra plants  
372 to temperate forests – continue to demonstrate that the direct uptake of GEM through the stomata of  
373 plant leaves is much more significant than previously thought.<sup>58-63</sup> Globally, litterfall containing GEM and  
374 throughfall, and not direct wet and dry deposition of oxidized Hg species, may represent the largest net  
375 flux of atmospheric Hg to terrestrial ecosystems, with estimates in the range of 1 - 2 kt/yr.<sup>59, 60, 64</sup>

376 The inconsistencies that remain in the evidence concerning the actual rates of historical mining  
377 emissions that affected the global atmosphere, soils and oceans, also impact the evidence supporting  
378 these revised estimates of oceanic and global Hg cycling. The three-fold reduction in Ag mining  
379 emissions by Zhang et al.<sup>5</sup> brought their modelled emission and deposition history closer to the world-  
380 wide lake sediment pattern (compared with the Streets et al.<sup>4,12</sup> emission inventories and atmospheric  
381 concentration calculations). However, the distinct bulge in modeled deposition during the late 19<sup>th</sup> and  
382 early 20<sup>th</sup> centuries is unlike the steadily increasing trend in lake sediment, peat and glacial ice Hg  
383 deposition (see Figs. 1 and S1), as well as in Arctic marine biota<sup>33</sup> during the same period. A further  
384 reduction in the mass of volatilized Hg from historical Ag and Hg production, which would not be  
385 inconsistent with the evidence discussed above, would bring the low emission scenario, and the natural  
386 archival records, into even closer agreement. There is recent evidence that further reductions may be  
387 justified. Guerrero's<sup>27</sup> analysis of reports from all global Ag mining jurisdictions between 1590 and 1895  
388 suggested a total global Hg release to air from Ag mining of just 6 kt. By comparison, Zhang et al.<sup>5</sup> and  
389 Streets et al.<sup>12</sup> estimated this release at 48 kt and 146 kt (most before 1920), respectively. These new

390 estimates urgently need further investigation as they have significant potential implications for our  
391 understanding of the anthropogenic component of the modern global Hg cycle and budget. If  
392 implemented in future models, the additional reductions would reduce the estimated amount of  
393 anthropogenic Hg in modern oceans and soils.

#### 394 **The Rate of Clearance of Anthropogenic Hg from the World's Oceans**

395 The differences between the alternate emission scenarios are associated with significant differences in  
396 the implied response times of the oceans to current emission reductions. All global ocean-atmosphere  
397 models predict that Hg clearance rates from most ocean basins will be slow relative to the rate of  
398 emission reductions in future, such that removal of anthropogenic Hg from the world's oceans will take  
399 many decades to centuries depending on the specific ocean basin and depth interval of the water mass  
400 in question, as well as the trajectory of emission controls.<sup>5, 7, 11, 20</sup> But according to Selin<sup>65</sup> and Engstrom  
401 et al.<sup>22</sup>, the high emission scenario predicts much slower and delayed reductions in environmental Hg  
402 levels following emission curbs than the low emissions scenario, because of the higher cumulative  
403 anthropogenic Hg totals in the environment, especially the oceans. Even at current global emission  
404 levels, there is a general scientific consensus that seawater and marine food chain Hg levels are likely to  
405 substantially increase over time, because of the slow clearance rate of Hg from the world's oceans  
406 coupled with additional legacy anthropogenic Hg released from soil and abandoned urban/industrial  
407 sources into rivers and revolatilized into the air.<sup>66</sup>

408 Until significant deficiencies in our current understanding of marine Hg cycling are resolved, especially  
409 for net ocean sediment burial rates and transformation rates between Hg species that influence the  
410 major sinks for seawater Hg (evasion to the atmosphere and burial in sediments), and greater  
411 consistency is achieved in the interpretation of natural archives of atmospheric Hg deposition, the  
412 prediction of the timeline and effects of global emission reductions will remain uncertain. It is clear,

413 however, that irrespective of these scientific uncertainties, emissions reductions are required to reverse  
414 the trend in oceanic anthropogenic Hg back towards natural levels, owing to the long response time of  
415 the subsurface ocean to changes in inputs.<sup>22, 65, 66</sup>

#### 416 **The Main Uncertainties in Global Hg Models and Budgets**

417 In this section, we summarize knowledge gaps and recommendations for further research stated in or  
418 developed from recent papers.<sup>5, 9, 13, 20, 22, 67-70</sup> Recommendations were selected on the basis of their  
419 relevance to global or oceanic models and budgets. Scientific uncertainties can be grouped under two  
420 headings: natural inputs and processes, and anthropogenic emissions.

#### 421 *Uncertainties in natural inputs and processes*

422 Net removal rates of anthropogenic Hg from the surface ocean are the result of competition between  
423 three simultaneously occurring natural processes: the particulate flux from the surface to the deep  
424 ocean (the 'biological pump', involving particle scavenging, remineralization and sedimentation); the  
425 mixing of surface and deep-ocean waters; and the net reduction of inorganic Hg(II) and subsequent  
426 evasion of Hg(0) back into the atmosphere<sup>11, 51</sup>. Some of the evaded Hg(0) is rapidly photo-oxidized in  
427 the lower troposphere and re-deposited to the ocean surface. Additional coupled ocean-atmosphere  
428 measurement studies are needed to comprehensively measure the concentrations of various Hg species  
429 spatially and temporally, and to better understand the transport and transformation rates of these co-  
430 occurring processes. The need is particularly acute in the Southern Hemisphere open oceans, as well as  
431 in regions where elevated anthropogenic Hg concentrations can be expected, such as the eastern  
432 equatorial Atlantic, eastern equatorial and high latitude Pacific, and northern Indian Oceans.

433 Uncertainties in the robustness of measurements of atmospheric and seawater Hg concentrations are  
434 exacerbated by relatively large inter-laboratory comparison errors, and so there is a particular need to  
435 improve the overall reliability of atmospheric and seawater Hg concentration and speciation

436 measurements. Few inter-comparison efforts have been mounted (see a review of atmospheric Hg  
437 determinations<sup>71</sup>). Past intercalibration exercises for seawater have only addressed total Hg, and the  
438 results have indicated significant discrepancies among the participating laboratories.<sup>72</sup> Future exercises  
439 should continue the effort of attaining reliable data, and should be extended to include all Hg species,  
440 even unstable species such as dimethyl Hg and dissolved Hg(0). The development of suitable seawater  
441 reference materials is encouraged.

442 The role of natural inputs in the global Hg budget is poorly constrained by measurements but potentially  
443 of major importance. If the actual rate of emissions from natural sources such as volcanoes, geothermal  
444 systems and marine hydrothermal vents is markedly higher or lower than currently thought, this would  
445 affect assumptions about the absolute amounts of, and relative balance between, natural and  
446 anthropogenic sources which are fundamental to our understanding of the global Hg cycle. Published  
447 estimates of global volcanic Hg emissions to air range over four orders of magnitude (0.1–1000 t/yr)<sup>73-77</sup>,  
448 with a recent summation of the literature estimating  $76 \pm 30$  t/yr from quiescent volcanic degassing, not  
449 including effusions or eruptions.<sup>77</sup> For oceans, the AMAP/UNEP report<sup>1</sup> estimated <0.6 kt/yr total Hg  
450 input from hydrothermal vents, which was based on few data and no systematic studies. Two recent  
451 GEOTRACES cruises in the North Atlantic and equatorial Pacific Oceans<sup>78, 79</sup> found conflicting evidence of  
452 an effect from vents on seawater Hg concentrations. Some shallow vents may release a substantial  
453 fraction of their emissions at the surface as gas bubbles containing GEM.<sup>80</sup> More direct observations of  
454 focused and diffuse-flow vent fluids, gases and hydrothermal plumes are needed to better constrain the  
455 Hg flux, and its contribution to the global Hg cycle.<sup>81</sup> Submarine groundwater discharges (SGDs) are also  
456 likely to bring important amounts of Hg into the ocean, but there are as yet insufficient data to quantify  
457 their inputs globally.<sup>82</sup> Several recent papers indicate that SGD inputs of Hg may be locally as important  
458 as atmospheric inputs, at least in some coastal environments.<sup>83-87</sup> Additionally, the recent findings of  
459 Zaferani et al.<sup>38</sup> that sediment burial fluxes of Hg in a region of high opal accumulation in Antarctica are

460 much higher than the average values used in our budget and in recent models points to the need to  
461 obtain better information on net Hg burial rates in ocean sediments, both in the coastal and deep  
462 oceans.

463 Given the importance of terrestrial soils as possibly the largest reservoir of natural and legacy  
464 anthropogenic Hg, global budget calculations will benefit from a better understanding of terrestrial Hg  
465 cycling.<sup>62</sup> The lack of knowledge on the actual reservoir size that may be interacting with other parts of  
466 the biosphere has been highlighted by Schuster et al.<sup>52</sup>, who suggested that Arctic permafrost soils are  
467 an under-appreciated major repository of Hg. Although permafrost Hg is mainly natural in origin, it could  
468 become an important part of the global Hg cycle in future. There is little understanding of precisely how  
469 much and how rapidly Hg releases from this source may grow with future climate warming, but they are  
470 expected to increase. Export of the stored Hg and organic matter could lead to greater MeHg production  
471 in northern aquatic ecosystems.<sup>88</sup> Other research priorities in this area include more measurements of  
472 the evasion rates of Hg from soils and the release rates of Hg to water following degradation of soil  
473 organic matter, as well as improvements in defining the foliar uptake Hg(0) pathway in global models.

#### 474 Uncertainties in anthropogenic emissions

475 The absolute amounts in historical emission inventories, and especially the role of Ag metal mining, have  
476 been questioned in recent work comparing model outputs with past Hg deposition rates, as  
477 reconstructed from natural archives of atmospheric deposition (see above). Some of the uncertainty lies  
478 with the natural archives. For example, a recent paper has shown that the Hg accumulation rates in a  
479 Tibetan Plateau glacier ice core were one to two orders of magnitude lower than in a nearby lake  
480 sediment, yet both archives yielded remarkably similar trends.<sup>42</sup> Similarly, the sediment, peat and ice  
481 core literature reviewed above displays similar Hg deposition trends over time, but different absolute  
482 fluxes, with ice cores exhibiting the lowest values of all possibly because of Hg photoreduction of  
483 deposited Hg(II) to Hg(0) and its revolatilization from snow surfaces.<sup>89</sup> Given the apparent importance

484 of historical deposition to current world Hg budgets and to future emission reduction scenarios, a  
485 concerted effort to understand the reasons for the different findings from peat, lake sediment and  
486 glacial ice archives is called for that would build upon earlier work.<sup>7, 54, 90, 91</sup> Arriving at an agreed  
487 historical emission amount from precious metal mining would eliminate much of the uncertainty  
488 surrounding current anthropogenic Hg inventories in soils and the oceans.

489  
490 The accuracy of the recent atmospheric emission inventories, including that of AMAP/UNEP<sup>1</sup>, has also  
491 been questioned in the literature, in part due to the inconsistency between the recent trends in primary  
492 industrial emissions, which are flat or rising, and the large (~30–40%) decreases in atmospheric GEM  
493 concentrations and wet deposition at background Northern Hemisphere monitoring stations since  
494 1990.<sup>22, 69</sup> Zhang et al.<sup>69</sup> found that primary industrial emissions and GEM trends were brought into  
495 closer agreement by accounting for the decline in Hg release from commercial products over this period,  
496 by reducing the assumed volatilization rate of Hg from present-day ASGM, and by accounting for the  
497 shift in Hg(0)/Hg(II) speciation of emissions from coal-fired utilities after implementation of gaseous  
498 pollutant control measures. Because the emission inventories are the basis of global modelling efforts,  
499 resolving this discrepancy should improve the accuracy of global budgets and future trend scenarios.  
500 ASGM emissions were the largest anthropogenic source of atmospheric Hg in recent years, according to  
501 AMAP/UNEP<sup>1</sup>, but this finding has been disputed.<sup>22, 69</sup> Verifiable and higher quality emission data from  
502 ASGM operations are therefore a priority need. Studies of the speciation and distribution of the Hg  
503 released into air, land and waters from present-day ASGM operations are also called for.

504  
505 The identified uncertainties and knowledge gaps described above should not be construed as  
506 undermining the rationale for the Minamata Convention on Mercury. All model and budget studies are  
507 in agreement that current levels of anthropogenic Hg emissions are likely to lead to increased



508 environmental exposure of wildlife and humans (albeit of varying magnitude in different species and  
509 settings), and that reducing these emissions is a necessity for reducing their negative environmental and  
510 health impacts. The uncertainties and knowledge gaps mainly affect our capability to predict where,  
511 when, and by how much, rather than if, the environment will respond to reduced emissions.

512

### 513 **Acknowledgements**

514 This paper was prepared as a contribution to the United Nations Environment Programme's 2018 Global  
515 Mercury Assessment, and we thank all of our colleagues who participated in this process, particularly G.  
516 Futsaeter and E. Toda (UNEP), S. Wilson (AMAP) and J. Munthe (IVL Swedish Environmental Research  
517 Institute). The work was financially supported by UNEP, and by support from the Geological Survey of  
518 Canada (G. Cotteret and B. Vigneault) to PMO. PMO was hosted by the Dept. of Geoscience, Aarhus  
519 University, during preparation of this paper. RPM's involvement was supported by NSF Chemical  
520 Oceanography grant # 1634048, and Wang's involvement by the Canada Research Chair program. S.  
521 Duckworth prepared the figures and C. Symon was copy editor. We kindly thank the following for access  
522 to their raw data: E. Beal, S. Kang, D. Streets, C. Zdanowicz, Y. Zhang, and J. Zheng.

523

### 524 **Supporting Information Available**

525 Figure S1 presents the two contrasting estimates of global anthropogenic Hg emissions to air, and  
526 associated atmospheric deposition to lakes through history as discussed in this review. Table S1  
527 contains supporting information relevant to the development of the global and ocean budgets. This  
528 information is available free of charge via the Internet at <http://pubs.acs.org>.

529 **References**

- 530 1. AMAP/UNEP *Technical Background Report for the Global Mercury Assessment 2013*; Arctic  
531 Monitoring and Assessment Programme, Oslo, Norway/UNEP Chemicals Branch, Geneva, Switzerland, 2013;  
532 p 263.
- 533 2. Fitzgerald, W. F.; Lamborg, C. H., Geochemistry of mercury in the environment. In *Treatise on*  
534 *Geochemistry, 2nd Ed*, Elsevier: 2014.
- 535 3. Amos, H. M.; Jacob, D. J.; Kocman, D.; Horowitz, H. M.; Zhang, Y.; Dutkiewicz, S.; Horvat, M.; Corbitt,  
536 E. S.; Krabbenhoft, D. P.; Sunderland, E. M., Global biogeochemical implications of mercury discharges from  
537 rivers and sediment burial. *Environ. Sci. Technol.* **2014**, *48*, 9514–9522.
- 538 4. Streets, D. G.; Devane, M. K.; Lu, Z.; Bond, T. C.; Sunderland, E. M.; Jacob, D. J., All-time releases of  
539 mercury to the atmosphere from human activities. *Environ. Sci. Technol.* **2011**, *45*, 10485–10491.
- 540 5. Zhang, Y.; Jaeglé, L.; Thompson, L.; Streets, D. G., Six centuries of changing oceanic mercury. *Global*  
541 *Biogeochem. Cycles* **2014**, *28*, 1251–1261.
- 542 6. Horowitz, H. M.; Jacob, D. J.; Amos, H. M.; Streets, D. G.; Sunderland, E. M., Historical mercury  
543 releases from commercial products: Global environmental implications. *Environ. Sci. Technol.* **2014**, *48*,  
544 10242–10250.
- 545 7. Amos, H. M.; Sonke, J. E.; Obrist, D.; Robins, N.; Hagan, N.; Horowitz, H. M.; Mason, R. P.; Witt, M.;  
546 Hedgecock, I. M.; Corbitt, E. S.; Sunderland, E. M., Observational and modeling constraints on global  
547 anthropogenic enrichment of mercury. *Environ. Sci. Technol.* **2015**, *49*, 4036–4047.
- 548 8. Paranjape, A. R.; Hall, B. D., Recent advances in the study of mercury methylation in aquatic systems.  
549 *Facets* **2017**, *2*, 85–119.
- 550 9. Sonke, J. E.; Heimbürger, L.-E.; Dommergue, A., Mercury biogeochemistry: Paradigm shifts,  
551 outstanding issues and research needs. *Comptes Rendus Geoscience* **2013**, *345*, 213–224.
- 552 10. AMAP/UNEP *Technical Background Assessment for the 2018 Global Mercury Assessment*; United  
553 Nations Environment Programme: Geneva, Switzerland, 2018; (in press).
- 554 11. Mason, R. P.; Choi, A. L.; Fitzgerald, W. F.; Hammerschmidt, C. R.; Lamborg, C. H.; Soerensen, A. L.;  
555 Sunderland, E. M., Mercury biogeochemical cycling in the ocean and policy implications. *Environ. Res.* **2012**,  
556 *119*, 101–117.
- 557 12. Streets, D. G.; Horowitz, H. M.; Jacob, D. J.; Lu, Z.; Levin, L.; ter Schure, A. F. H.; Sunderland, E. M.,  
558 Total mercury released to the environment by human activities. *Environ. Sci. Technol.* **2017**, *51*, 5969–5977.
- 559 13. Amos, H. M.; Jacob, D. J.; Streets, D. G.; Sunderland, E. M., Legacy impacts of all-time anthropogenic  
560 emissions on the global mercury cycle. *Global Biogeochem. Cycles* **2013**, *27*, 410–421.
- 561 14. Guerrero, S., Chemistry as a tool for historical research: Identifying paths of historical mercury  
562 pollution in the Hispanic New World. *Bull. Hist. Chem.* **2012**, *37*, 61–70.
- 563 15. Guerrero, S., The history of silver refining in New Spain, 16C to 18C: back to the basics. *Hist. Technol.*  
564 **2016**, *32*, 2–32.
- 565 16. Fitzgerald, W. F.; Engstrom, D. R.; Mason, R. P.; Nater, E. A., The case for atmospheric mercury  
566 contamination in remote areas. *Environ. Sci. Technol.* **1998**, *32*, 1–7.
- 567 17. Correla, J. P.; Valero-Garces, B. L.; Wang, F.; Martínez-Cortizas, A.; Cuevas, C. A.; Saiz-Lopez, A., 700  
568 years reconstruction of mercury and lead atmospheric deposition in the Pyrenees (NE Spain). *Atmos.*  
569 *Environ.* **2017**, *155*, 97–107.
- 570 18. Zhang, Y.; Jaeglé, L.; Thompson, L., Natural biogeochemical cycle of mercury in a global three-  
571 dimensional ocean tracer model. *Global Biogeochem. Cycles* **2014**, *28*, 553–570.
- 572 19. Driscoll, C. T.; Mason, R. P.; Chan, H. M.; Jacob, D. J.; Pirrone, N., Mercury as a global pollutant:  
573 sources, pathways, and effects. *Environ. Sci. Technol.* **2013**, *47*, 4967–4983.
- 574 20. Lamborg, C. H.; Hammerschmidt, C. R.; Bowman, K. L.; Swarr, G. J.; Munson, K. M.; Ohnemus, D. C.;  
575 Lam, P. J.; Heimbürger, L.-E.; Rijkenberg, M. J. A.; Saito, M. A., A global ocean inventory of anthropogenic  
576 mercury based on water column measurements. *Nature* **2014**, *512*, 65–68.

- 577 21. Enrico, M.; Le Roux, G.; Heimbürger, L. E.; Van Beek, P.; Souhaut, M.; Chmeleff, J.; Sonke, J. E.,  
578 Holocene atmospheric mercury levels reconstructed from peat bog mercury stable isotopes. *Environ. Sci.*  
579 *Technol.* **2017**, *51*, 5899–5906.
- 580 22. Engstrom, D. R.; Fitzgerald, W. F.; Cooke, C. A.; Lamborg, C. H.; Drevnick, P. E.; Swain, E. B.; Balogh, S.  
581 J.; Balcom, P. H., Atmospheric Hg emissions from preindustrial gold and silver extraction in the Americas: A  
582 reevaluation from lake-sediment archives. *Environ. Sci. Technol.* **2014**, *48*, 6533–6543.
- 583 23. Nriagu, J. O., Legacy of mercury pollution. *Nature* **1993**, *363*, 589.
- 584 24. Nriagu, J. O., Mercury pollution from the past mining of gold and silver in the Americas. *Sci. Total*  
585 *Environ.* **1994**, *149*, 167–181.
- 586 25. Strode, S.; Jaegle, L.; Selin, N. E., Impact of mercury emissions from historic gold and silver mining:  
587 Global modeling. *Atmos. Environ.* **2009**, *43*, 2012–2017.
- 588 26. TePaske, J. J.; Brown, K. W., *A New World of Gold and Silver*. Brill: Leiden, 2010.
- 589 27. Guerrero, S. *The environmental history of silver production, and its impact on the United Nations*  
590 *Minimata Convention on mercury*; Extended Abstract, Session on Global Production and Distribution of  
591 Silver, World Economic History Congress, Boston, USA, July 29 - August 3, 2018. Available at:  
592 <http://wehc2018.org/wp-content/uploads/2018/04/WEHCguerreroMinamata-2.pdf>: 2018.
- 593 28. Director of U.S. Mint *Annual Report of the Director of the U.S. Mint for the Fiscal Year Ended June*  
594 *1944, including Report on the Production of Precious Metals During the Calendar Year 1943*; Treasury Dept.  
595 Doc. 3133, U.S. Govt. Printing Office: Washington, 1945; p 101.
- 596 29. Sillitoe, R., Supergene silver enrichment reassessed. In *Supergene Environments, Processes and*  
597 *Products*, Titley, S. R., Ed. Society of Economic Geologists, Spec. Pub. 14: 2009; pp 15–32.
- 598 30. Guerrero, S., *Silver by Fire, Silver by Mercury: A Chemical History of Silver Refining in New Spain and*  
599 *Mexico, 16th to 19th Centuries*. Brill: Leiden, the Netherlands, 2017.
- 600 31. Johnson, D. A.; Whittle, K., The chemistry of the Hispanic-American amalgamation process. *J. Chem.*  
601 *Soc. Dalton Trans.* **1999**, 4239–4243.
- 602 32. Streets, D. G.; Lu, Z.; Levin, L.; ter Schure, A. F. H.; Sunderland, E. M., Historical releases of mercury to  
603 air, land, and water from coal combustion. *Sci. Total Environ.* **2018**, *615*, 131–140.
- 604 33. Dietz, R.; Outridge, P. M.; Hobson, K. A., Anthropogenic contributions to mercury levels in present-  
605 day Arctic animals - A review. *Sci. Total Environ.* **2009**, *407*, 6120–6131.
- 606 34. Copan, L.; Fowles, J.; Barreau, T.; McGee, N., Mercury toxicity and contamination of households from  
607 the use of skin creams adulterated with mercurous chloride (calomel). *Int. J. Environ. Res. Publ. Health* **2015**,  
608 *12*, 10943–10954.
- 609 35. Shotyk, W.; Goodsite, M. E.; Roos-Barracough, F.; Givélet, N.; Le Roux, G.; Weiss, D.; Cheburkin, A.  
610 K.; Knudsen, K.; Heinmeier, J.; van Der Knaap, W. O.; Norton, S. A.; Lohse, C., Accumulation rates and  
611 predominant atmospheric sources of natural and anthropogenic Hg and Pb on the Faroe Islands. *Geochim.*  
612 *Cosmochim. Acta* **2005**, *69*, 1–17.
- 613 36. Roos-Barracough, F.; Givélet, N.; Cheburkin, A. K.; Shotyk, W.; Norton, S. A., Use of Br and Se in peat  
614 to reconstruct the natural and anthropogenic fluxes of atmospheric Hg: a 10, 000-year record from Caribou  
615 Bog, Maine. *Environ. Sci. Technol.* **2006**, *40*, 3188–3194.
- 616 37. Roos-Barracough, F.; Shotyk, W., Millennial-scale records of atmospheric mercury deposition  
617 obtained from ombrotrophic and minerotrophic peatlands in the Swiss Jura Mountains. *Environ. Sci. Technol.*  
618 **2003**, *37*, 235–244.
- 619 38. Zaferani, S.; Pérez-Rodríguez, M.; Biester, H., Diatom ooze – a large marine mercury sink. *Science*  
620 **2018**, 10.1126/science.aat2735.
- 621 39. Fitzgerald, W. F.; Engstrom, D. R.; Hammerschmidt, C. R.; Lamborg, C. H.; Balcom, P. H.; Lima-Braun,  
622 A. L.; Bothner, M. H.; Reddy, C. M., Global and local sources of mercury deposition in coastal New England  
623 reconstructed from a multiproxy, high-resolution, estuarine sediment record. *Environ. Sci. Technol.* **2018**, *52*,  
624 7614–7620.

- 625 40. Beal, S. A.; Osterberg, E. C.; Zdanowicz, C. M.; Fisher, D. A., Ice core perspective on mercury pollution  
626 during the past 600 years. *Environ. Sci. Technol.* **2015**, *49*, 7641–7647.
- 627 41. Zheng, J., Archives of total mercury reconstructed with ice and snow from Greenland and the  
628 Canadian High Arctic. *Sci. Total Environ.* **2015**, *509–510*, 133–144.
- 629 42. Kang, S.; Huang, J.; Wang, F.; Zhang, Q.; Zhang, Y.; Li, C.; Wang, L.; Chen, P.; Sharma, C.; Li, Q.;  
630 Sillanpää, M.; Hou, J.; Xu, B.; Guo, J., Atmospheric mercury depositional chronology reconstructed from lake  
631 sediment and ice cores in the Himalayas and Tibetan Plateau. *Environ. Sci. Technol.* **2016**, *50*, 2859–2869.
- 632 43. Chellman, N.; McConnell, J. R.; Arienzo, M.; Pederson, G. T.; Aarons, S. M.; Csank, A., Reassessment  
633 of the Upper Fremont Glacier ice-core chronologies by synchronizing of ice-core-water isotopes to a nearby  
634 tree-ring chronology. *Environ. Sci. Technol.* **2017**, *51*, 4230–4238.
- 635 44. Cooke, C. A.; Hintelmann, H.; Ague, J. J.; Burger, R.; Biester, H.; Sachs, J. P.; Engstrom, D. R., Use and  
636 legacy of mercury in the Andes. *Environ. Sci. Technol.* **2013**, *47*, 4181–4188.
- 637 45. Obrist, D.; Pearson, C.; Webster, J.; Kane, K.; Lin, C. J.; Aiken, G. R.; Alpers, C. N., A synthesis of  
638 terrestrial mercury in the western United States: Spatial distribution defined by land cover and plant  
639 productivity. *Sci. Total Environ.* **2016**, *568*, 522–535.
- 640 46. Pacyna, J. M.; Travnikov, O.; De Simone, F.; Hedgecock, I. M.; Sundseth, K.; Pacyna, E. G.;  
641 Steenhuisen, F.; Pirrone, N.; Munthe, J.; Kindbom, K., Current and future levels of mercury atmospheric  
642 pollution on a global scale. *Atmos. Chem. Phys.* **2016**, *16*, 12495–12511.
- 643 47. Cohen, M. D.; Draxler, R. R.; Artz, R. S.; Blanchard, P.; Gustin, M. S.; Han, Y.-J.; Holsen, T. M.; Jaffe, D.  
644 A.; Kelley, P.; Lei, H.; Loughner, C. P.; Luke, W. T.; Lyman, S. N.; Niemi, D.; Pacyna, J. M.; Pilote, M.; Poissant,  
645 L.; Ratte, D.; Ren, X.; Steenhuisen, F.; Steffen, A.; Tordon, R.; S.J., W., Modeling the global atmospheric  
646 transport and deposition of mercury to the Great Lakes. *Elementa* **2016**, *4*, 000118.
- 647 48. Liu, M.; Chen, L.; Wang, X.; Zhang, W.; Tong, Y.; Ou, L.; Xie, H.; Shen, H.; Ye, X.; Deng, C.; Wang, H.,  
648 Mercury export from mainland China to adjacent seas and its influence on the marine mercury balance.  
649 *Environ. Sci. Technol.* **2016**, *50*, 6224–6232.
- 650 49. Kocman, D.; Wilson, S. J.; Amos, H. A.; Telmer, K. H.; Steenhuisen, F.; Sunderland, E. M.; Mason, R. P.;  
651 Outridge, P.; Horvat, M., Toward an assessment of the global inventory of present-day mercury releases to  
652 freshwater environments. *Int. J. Environ. Res. Public Health* **2017**, *14*, doi:10.3390/ijerph14020138.
- 653 50. Mason, R. P.; Hammerschmidt, C. R.; Lamborg, C. H.; Bowman, K. L.; Swarr, G. J.; Shelley, R. U., The  
654 air-sea exchange of mercury in the low latitude Pacific and Atlantic Oceans. *Deep-Sea Res.* **2017**, *122*, 17–28.
- 655 51. Sunderland, E. M.; Mason, R. P., Human impacts on open ocean mercury concentrations. *Global*  
656 *Biogeochem. Cycles* **2007**, *21*, doi:10.1029/2006GB002876.
- 657 52. Schuster, P. F.; Schaefer, K. M.; Aiken, G. R.; Antweiler, R. C.; Dewild, J. F.; Gryziec, J. D.; Gusmeroli,  
658 A.; Hugelius, G.; Jafarov, E.; Krabbenhoft, D. L.; Liu, L.; Herman-Mercer, N.; Mu, C.; Roth, D. A.; Schaefer, T.;  
659 Striegel, R. G.; Wickland, K. P.; Zhan, T., Permafrost stores a globally significant amount of mercury. *Geophys.*  
660 *Res. Lett.* **2018**, *45*, 10.1002/2017GL075571.
- 661 53. Mason, R. P.; Fitzgerald, W. F.; Morel, F. M. M., The biogeochemical cycling of elemental mercury:  
662 Anthropogenic influences. *Geochim. Cosmochim. Acta* **1994**, *58*, 3191–3198.
- 663 54. Lamborg, C. H.; Fitzgerald, W. F.; O'Donnell, J.; Torgerson, T., A non-steady-state compartmental  
664 model of global-scale mercury biogeochemistry with interhemispheric gradients. *Geochim. Cosmochim. Acta*  
665 **2002**, *66*, 1105–1118.
- 666 55. Selin, N. E.; Jacob, D. J.; Yantosca, R. M.; Strode, S.; Jaeglé, L.; Sunderland, E. M., Global 3-D land-  
667 ocean-atmosphere model for mercury: present day versus preindustrial cycles and anthropogenic  
668 enrichment factors for deposition. *Global Biogeochem. Cycles* **2008**, *22*, GB2011.
- 669 56. Soerensen, A. L.; Sunderland, E. M.; Holmes, C. D.; Jacob, D. J.; Yantosca, R. M.; Skov, H.; Christensen,  
670 J. H.; Strode, S. A.; Mason, R. P., An improved global model for air-sea exchange of mercury: High  
671 concentrations over the North Atlantic. *Environ. Sci. Technol.* **2010**, *44*, 8574–8580.

- 672 57. Strode, S.; Jaegle, L.; Emerson, S., Vertical transport of anthropogenic mercury in the ocean. *Global*  
673 *Biogeochem. Cycles* **2010**, *24*, GB4014.
- 674 58. Enrico, M.; Le Roux, G.; Maruszczak, N.; Heimbürger, L. E.; Claustres, A.; Fu, X.; Sun, R.; Sonke, J. E.,  
675 Atmospheric mercury transfer to peat bogs dominated by gaseous elemental mercury dry deposition.  
676 *Environ. Sci. Technol.* **2016**, *50*, 2405–2412.
- 677 59. Fu, X.; Zhu, W.; Zhang, H.; Sommar, J.; Yu, B.; Yang, X.; Wang, X.; Lin, C.-J.; Feng, X., Depletion of  
678 atmospheric gaseous elemental mercury by plant uptake at Mt. Changbai, Northeast China. *Atmos. Chem.*  
679 *Phys.* **2016**, *16*, 12861–12873.
- 680 60. Wang, X.; Bao, Z.; Lin, C. J.; Yuan, W.; Feng, X., Assessment of global mercury deposition through  
681 litterfall. *Environ. Sci. Technol.* **2016**, *50*, 8548–8557.
- 682 61. Obrist, D.; Agnan, Y.; Jiskra, M.; Olson, C. L.; Colegrove, D. P.; Hueber, J.; Moore, C. W.; Sonke, J. E.;  
683 Helmig, D., Tundra uptake of atmospheric elemental mercury drives Arctic mercury pollution. *Nature* **2017**,  
684 *547*, 201–204.
- 685 62. Obrist, D.; Kirk, J. L.; Zhang, L.; Sunderland, E. M.; Jiskra, M.; Selin, N. E., A review of global  
686 environmental mercury processes in response to human and natural perturbations: Changes of emissions,  
687 climate, and land use. *Ambio* **2018**, *47*, 116–140.
- 688 63. Risch, M. R.; De Wild, J. F.; Gay, D. A.; Zhang, L.; Boyer, E. W.; Krabbenhoft, D. P., Atmospheric  
689 mercury deposition to forests in the eastern USA. *Environ. Pollut.* **2017**, *228*, 8–18.
- 690 64. Jiskra, M.; Sonke, J. E.; Obrist, D.; Bieser, J.; Ebinghaus, R.; Myhre, C. L.; Pfaffhuber, K. A.; Wängberg,  
691 I.; Kyllönen, K.; Worthy, D.; Martin, L. G.; Labuschagne, C.; Mkololo, T.; Ramonet, M.; Magand, O.;  
692 Dommergue, A., A vegetation control on seasonal variations in global atmospheric mercury concentrations.  
693 *Nature Geosci.* **2018**, *11*, 244–250.
- 694 65. Selin, N. E., Global change and mercury cycling: Challenges for implementing a global mercury treaty.  
695 *Environ. Toxicol. Chem.* **2014**, *33*, 1202–1210.
- 696 66. Sunderland, E. M.; Selin, N. E., Future trends in environmental mercury concentrations: implications  
697 for prevention strategies. *Environ. Health* **2013**, *12*.
- 698 67. Lamborg, C. H.; Hammerschmidt, C. R.; Bowman, K. L., An examination of the role of particles in  
699 oceanic mercury cycling. *Phil. Trans. Royal Soc. A* **2016**, *374*, 2081.
- 700 68. Song, S.; Selin, N. E.; Soerensen, A. L.; Angot, H.; Artz, R.; Brooks, S.; Brunke, E.; Conley, G.;  
701 Dommergue, A.; Ebinghaus, R.; Holsen, T.; Kang, S.; Kelley, P.; Luke, W.; Magand, O.; Marumoto, K.;  
702 Pfaffhuber, K. A.; Ren, X.; Zhang, Q., Top-down constraints on atmospheric mercury emissions and  
703 implications for global biogeochemical cycling. *Atmos. Chem. Phys.* **2015**, *15*, 7103–7125.
- 704 69. Zhang, Y.; Jacob, D. J.; Horowitz, H. M.; Chen, L.; Amos, H. M.; Krabbenhoft, D. P.; Slemr, F.; St. Louis,  
705 V. L.; Sunderland, E. M., Observed decrease in atmospheric mercury explained by global decline in  
706 atmospheric emissions. *Proc. Nat. Acad. Sci.* **2016**, *113*, 201516312.
- 707 70. Kwon, S. Y.; Selin, N. E., Uncertainties in atmospheric mercury modeling for policy evaluation.  
708 *Current Pollut. Rep.* **2016**, *2*, 103–114.
- 709 71. Gustin, M. S.; Amos, H. M.; Huang, J.; Miller, M. B.; Heidecorn, K., Measuring and modeling mercury  
710 in the atmosphere: a critical review. *Atmos. Chem. Phys.* **2015**, *15*, 5697–5713.
- 711 72. Lamborg, C. H.; Hammerschmidt, C. R.; Gill, G. A.; Mason, R. P.; Gichuki, S., An intercomparison of  
712 procedures for the determination of total mercury in seawater and recommendations regarding mercury  
713 speciation during GEOTRACES cruises. *Limnol. Oceanogr. Methods* **2012**, *10*, 90–100.
- 714 73. Nriagu, J. O., A global assessment of natural sources of atmospheric trace metals. *Nature* **1989**, *338*,  
715 47–49.
- 716 74. Nriagu, J.; Becker, C., Volcanic emissions of mercury to the atmosphere: global and regional  
717 inventories. *Sci. Total Environ.* **2003**, *304*, 3–12.
- 718 75. Ferrara, R.; Mazzolai, B.; Lanzillotta, E.; Nucaro, E.; Pirrone, N., Volcanoes as emission sources of  
719 atmospheric mercury in the Mediterranean basin. *Sci. Total Environ.* **2000**, *259*, 115–121.

- 720 76. Pyle, D. M.; Mather, T. A., The importance of volcanic emissions for the global atmospheric mercury  
721 cycle. *Atmos. Environ.* **2003**, *37*, 5115–5124.
- 722 77. Bagnato, E.; Tamburello, G.; Avarod, G.; Martinez-Cruz, M.; Enrico, M.; Fu, X.; Sprovieri, M.; Sonke, J.  
723 E., Mercury fluxes from volcanic and geothermal sources: an update. In *The Role of Volatiles in the Genesis,  
724 Evolution and Eruption of Arc Magmas*, Zellmer, G. F.; Edmonds, M.; Straub, S. M., Eds. Geological Society:  
725 London, 2015; Vol. Special Publications, 410, p doi: 10.1144/SP410.2.
- 726 78. Bowman, K. L.; Hammerschmidt, C. R.; Lamborg, C. H.; Swarr, G. J., Mercury in the North Atlantic  
727 Ocean: The U.S. GEOTRACES zonal and meridional sections. *Deep Sea Res II* **2015**, *116*, 251–261.
- 728 79. Bowman, K. L.; Hammerschmidt, C. R.; Lamborg, C. H.; Swarr, G. J.; Agather, A. M., Distribution of  
729 mercury species across a zonal section of the eastern tropical South Pacific Ocean (U.S. GEOTRACES GP16).  
730 *Mar. Chem.* **2016**, *186*, 156–166.
- 731 80. Astakhov, A. S.; Ivanov, M. V.; Li, B. Y., Hydrochemical and atmochemical mercury dispersion zones  
732 over hydrothermal vents of the submarine Piip Volcano in the Bering Sea. *Oceanology* **2011**, *51*, 826–835.
- 733 81. German, C. R.; Casciotti, K. A.; Dutay, J. C.; Heimbürger, L. E.; Jenkins, W. J.; Measures, C. I.; Mills, R.  
734 A.; Obata, H.; Schlitzer, R.; Tagliabue, A.; Turner, D. R.; Whitby, H., Hydrothermal impacts on trace element  
735 and isotope ocean biogeochemistry. *Phil. Trans. Royal Soc. A* **2016**, *374*, 2081.
- 736 82. Moore, W. S., The effect of submarine groundwater discharge on the ocean. *Ann. Rev. Mar. Sci.*  
737 **2010**, *2*, 59–88.
- 738 83. Bone, S. E.; Charette, M. A.; Lamborg, C. H.; Gonnee, M. E., Has submarine groundwater discharge  
739 been overlooked as a source of mercury to coastal waters? *Environ. Sci. Technol.* **2007**, *41*, 3090–3095.
- 740 84. Black, F. J.; Paytan, A.; Knee, K. L.; De Sieyes, N. R.; Ganguli, P. M.; Gary, E.; Flegal, A. R., Submarine  
741 groundwater discharge of total mercury and monomethylmercury to central California coastal waters.  
742 *Environ. Sci. Technol.* **2009**, *43*, 5652–5659.
- 743 85. Ganguli, P. M.; Conaway, C. H.; Swarzenski, P. W.; Izbicki, J. A.; Flegal, A. R., Mercury speciation and  
744 transport via submarine groundwater discharge at a southern California coastal lagoon system. *Environ. Sci.*  
745 *Technol.* **2012**, *42*, 1480–1488.
- 746 86. Lee, Y.-G.; Rahman, M. D. M.; Kim, G.; Han, S., Mass balance of total mercury and  
747 monomethylmercury in coastal embayments of a volcanic island: significance of submarine groundwater  
748 discharge. *Environ. Sci. Technol.* **2011**, *45*, 9891–9900.
- 749 87. Laurier, F. J. G.; Cossa, D.; Beucher, C.; Breviere, E., The impact of groundwater discharges on  
750 mercury partitioning, speciation and bioavailability to mussels in a coastal zone. *Mar. Chem.* **2007**, *104*, 143–  
751 155.
- 752 88. Stern, G. A.; Macdonald, R. W.; Outridge, P. M.; Wilson, S.; Chetelat, J.; Cole, A.; Hintelmann, H.;  
753 Loseto, L. L.; Steffen, A.; Wang, F.; Zdanowicz, C., How does climate change influence arctic mercury? *Sci.*  
754 *Total Environ.* **2012**, *414*, 22–42.
- 755 89. Douglas, T. A.; Loseto, L. L.; Macdonald, R. W.; Outridge, P.; Dommergue, A.; Poulain, A.; Amyot, M.;  
756 Barkay, T.; Berg, T.; Chetelat, J.; Constant, P.; Evans, M.; Ferrari, C.; Gantner, N.; Johnson, M. S.; Kirk, J.;  
757 Kroer, N.; Larose, C.; Lean, D.; Nielsen, T. G.; Poissant, L.; Rognerud, S.; Skov, H.; Sorensen, S.; Wang, F.;  
758 Wilson, S.; Zdanowicz, C. M., The fate of mercury in Arctic terrestrial and aquatic ecosystems, a review.  
759 *Environ. Chem.* **2012**, *9*, 321–355.
- 760 90. Biester, H.; Bindler, R.; Martinez-Cortizas, A.; Engstrom, D. R., Modeling the past atmospheric  
761 deposition of mercury using natural archives. *Environ. Sci. Technol.* **2007**, *41*, 4851–4860.
- 762 91. Outridge, P. M.; Rausch, N.; Percival, J. B.; Shotyk, W.; McNeely, R., Comparison of mercury and zinc  
763 profiles in peat and lake sediment archives with historical changes in emissions from the Flin Flon metal  
764 smelter, Manitoba, Canada. *Sci. Total Environ.* **2011**, *409*, 548–563.
- 765

Table 1. Recent estimates of total, anthropogenic and 'natural' Hg masses in global air, soils and oceans (data in kilotonnes).

	Mason et al. <sup>11</sup> ; AMAP/UNEP <sup>1</sup>	Amos et al. <sup>13</sup>	Zhang et al. <sup>5</sup>	Lamborg et al. <sup>20</sup>	Present study <sup>b</sup>
Atmospheric Hg					
Total	5.1	5.3	4.4	n/a	4.4
Anthropogenic	3.4–4.1	4.6	3.6	n/a	3.6
Natural	1.0–1.7	0.7	0.8	n/a	0.8
Soil Hg (organic layers)					
Total	201	271	n/a	n/a	150
Anthropogenic	40	89	92	n/a	20
Natural	161	182	n/a	n/a	130
Oceanic Hg					
Total	358	343	257	316	313
Anthropogenic	53	222	66 (38–106) <sup>c</sup>	58±16 <sup>d</sup>	55
Natural	305	122	191	258 <sup>e</sup>	258

767 <sup>a</sup> The time point for designation of the 'natural' Hg state, and thus the quantification of 'natural' and 'anthropogenic' Hg masses, differed  
768 between studies: 2000 BC in the 'pre-anthropogenic period'<sup>13</sup>; prior to 1450 AD<sup>5, 18</sup> which preceded New World Ag, Au and Hg production; and  
769 about 1840 AD<sup>20</sup> which was prior to the North American Gold Rush and the expansion of coal-fired combustion sources. The anthropogenic Hg  
770 values from Mason et al.<sup>11</sup> and Lamborg et al.<sup>20</sup> are based on increases over the past ~100 to 150 years, and thus their 'natural' Hg masses may  
771 be over-estimated and the anthropogenic masses under-estimated compared with the other studies. <sup>b</sup> estimates for this assessment modified  
772 from Zhang et al.<sup>5</sup> as described in text, and thus the anthropogenic values represent the impact of human activities since 1450 AD. <sup>c</sup> uncertainty  
773 range shown in brackets. <sup>d</sup> based on an oceanic anthropogenic Hg:anthropogenic CO<sub>2</sub> ratio for 1994; a more recent (higher) oceanic CO<sub>2</sub>  
774 estimate gave an anthropogenic Hg estimate of 76 kt Hg.<sup>20</sup> <sup>e</sup> calculated by subtraction. n/a = not available.

**Figure Captions**

Figure 1. Glacial ice core records of atmospheric Hg deposition from (a) Mount Logan, Yukon<sup>40</sup>, (b) Mount Geladaindong, Tibetan Plateau, China<sup>42</sup>, and (c) the NEEM site, Greenland<sup>41</sup>, compared with (d) the global atmospheric emission history since 1850 AD.<sup>12</sup> Ice core Hg data are displayed: in (a) as mean $\pm$  SD values; in (b) and (c) as 3-point running averages. In all ice core plots, the solid red lines indicate decadal median values calculated from raw data. In (d), atmospheric emissions from Hg (cinnabar) refining and Ag mining operations are shown separately from all other anthropogenic sources (“other”).

Figure 2. Updated global Hg budget showing the anthropogenic impact on the Hg cycle since the pre-anthropogenic period (prior to 1450 AD). (See text for explanation of budget derivation. Ranges (where available) are given in brackets after the best estimate values; percentages in brackets represent the estimated increase in mass or flux due to human activities since the pre-anthropogenic period. Mass units in kilotonnes (kt), fluxes in kilotonnes per year (kt/y)).

Figure 3. Natural and anthropogenic Hg fluxes and masses in the world’s oceans. (Masses in kilotonnes (kt), and fluxes in (kt/y). Data adapted and revised from Zhang et al.<sup>5</sup>, based on the revised global budget shown in Fig. 2. Natural fluxes and masses in black, anthropogenic in red).









