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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

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

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by

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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 16th - late 19th 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27 historical documents on Ag production, and comparison of the scenarios against atmospheric Hg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 ± 0.5 kt/y. The
32 increase in atmospheric Hg concentrations has driven a $\sim 300\%$ 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 ($\sim 15\%$) 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.^{1,2} 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.^{2,3} 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.⁴⁻⁷ 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.² 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^{8,9}, 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) 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 report¹ 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.¹⁰

67 **A General Overview of Recent Advances**

68 In the technical background report to the 2013 Global Mercury Assessment¹, based on a global budget
69 developed by Mason et al.¹¹, it was estimated that human activities had increased atmospheric Hg
70 concentrations by 300–500% since about the end of the 19th 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^{4, 7, 12, 13} have emphasized the point that the end of the 19th 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 16th century onwards^{14, 15}, and re-examination of the atmospheric Hg fluxes recorded in
80 long lake sediment and peat cores covering most of the last millennium⁷, indicate that significant
81 amounts of Hg were emitted by human activities in the period after the 16th century, and before the
82 mid-19th century when the “pre-industrial period” is often regarded as having ended (e.g.,^{16, 17}). There
83 are different definitions of a time that represents truly natural or ‘pre-anthropogenic’ conditions: e.g.,
84 2000 BC¹³, 3000 BC to 1550 AD⁷, or prior to 1450 AD.¹⁸ For the purposes of this review we adopted
85 Zhang et al.’s⁵ 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.¹ 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^{4-7, 12, 13,}
91 ¹⁸⁻²⁰. Major uncertainties persist, however, especially in estimates of the amount of anthropogenic Hg in
92 the oceans (cf. ^{5, 13}).

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%⁵ to 660%¹³, 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.⁵ 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.¹³, 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.²¹ reported that maximum 20th 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.^{2, 16, 22} Amos et al.⁷ attributed the lower estimates to
109 an erroneous selection of natural deposition values that were too high, because they were based on 18th

110 and early 19th 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 19th 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^{5, 13} 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 16th and late 19th 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.'s⁴ all-time emission inventory, with Zhang et al.⁵ 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.⁵ and Amos et al.,¹³
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).^{15, 23-25} 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.'s¹² 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 16th to 19th 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.¹⁴ 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.¹⁵ 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.²⁶ 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.^{5,7,27}

154 Streets et al.'s^{4,12} 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^{23, 24} 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.^{14, 15, 27} 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.^{27, 28} 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, Ag₂S) with
166 silver chloride in varying proportions.^{15, 29} 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.³⁰ The AgHg amalgam was then heated to remove the Hg. These
170 Spanish colonial practices were later employed during the 19th century North American Gold Rush,
171 except that iron was added to the chemical slurry to reduce Hg loss to insoluble calomel (Hg₂Cl₂).²⁷ In
172 the refining process, the major cause of Hg loss was calomel formation, with minimal volatile emissions
173 even during the heating stage.^{27, 30} 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.³¹ 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, Guerrero¹⁴
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 19th century, numerous sources reported Hg losses to air of less than
185 1% of the Hg consumed by refining^{15, 27, 30}, 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 report¹ 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 ASGM³⁰, 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 Guerrero¹⁴, Zhang et al.⁵ adopted a low emission factor of 17% for Hg from Spanish colonial
198 and 19th century Gold Rush Ag mining. The resulting all-time cumulative anthropogenic emissions to air
199 (190 kt⁵) were just over half those estimated by Streets et al.⁴ 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 kt¹²
204 was even higher than Streets et al.,⁴ because of added commercial product emissions after the late
205 19th century⁶, 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.²² of
208 another large global set of lake sediment Hg profiles independent from those in Zhang et al.⁵. 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.²²

215 Similarly, there is little evidence in natural archives to support a major atmospheric Hg impact from late
216 19th century North American Gold Rush mining. Streets et al.'s⁴ 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 20th 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 onwards⁶ did not substantially diminish the late 19th century
221 peak in emissions and atmospheric concentrations (see¹²). 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 20th century in the same core profiles.^{5, 22, 25} Thus, the world-wide lake sediment record appears to
224 suggest a negligible global impact from Ag, Hg and Au production during the 16th to early 20th centuries.
225 Coincident increases in atmospheric emissions from other sources such as coal combustion and

226 commercial Hg uses^{12, 32} may have contributed to the steady increase of Hg in world-wide deposition
227 (see above) and in Arctic marine biota³³ that started in the latter half of the 19th century.

228 Amos et al.⁷ 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.⁷ also proposed that the Guerrero¹⁴ 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 sunlight³⁴, 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.⁷ 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.⁷ 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.⁴, 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 Strobe et al.²⁵, Engstrom et al.²² and Zhang et al.⁵
243 were supported by peat bog studies from the Faroe Islands³⁵, Maine, USA³⁶, Swiss Jura Mountains³⁷ and
244 the Pyrenees²¹ that all showed relatively muted Hg increases prior to 1900, and with 20th century
245 accumulation rates substantially higher than in the late 19th century. Recently published high-resolution
246 marine sediment cores from a remote region in the Southern Ocean³⁸, and off New England, USA³⁹,
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 1890¹², three ice cores displayed increases in
252 Hg accumulation between 1840-60 and 1880-1900 of 40 to 150% (reanalysis of data from refs. ⁴⁰⁻⁴²). 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 20th century.⁴⁰ 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.⁴³

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^{17,44},
266 although these effects are not seen everywhere (e.g. ⁴³).

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

268 Here we present the updated budgets included in the 2018 AMAP/UNEP report¹⁰, explain how they
269 were developed, and specify how the two main contrasting views of the world's historical emissions^{5,7,13}
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^{1,11} with results from Zhang et al.'s model⁵ 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.¹³ and
275 Zhang et al.⁵ agreed to within about 30% of the estimates in the AMAP/UNEP budget¹ (Table 1). We
276 accepted Zhang et al.'s⁵ 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.¹¹ 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 literature¹⁸⁻²⁰, 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.'s³⁸ 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.⁴⁵

293 The new terrestrial reservoir and flux estimates (see Table 1 and Fig. 2) were updated from Driscoll et
294 al.¹⁹ and Amos et al.⁷ Specific fluxes were also adopted from Pacyna et al.⁴⁶ and Cohen et al.⁴⁷, 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/UNEP¹ 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.¹³ and Zhang et al.⁵ suggested that soils globally contain more anthropogenic Hg than
299 was stated in AMAP/UNEP¹, 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.⁵, Liu et al.⁴⁸, and Kocman et al.⁴⁹

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,¹ and using the relative anthropogenic:natural flux estimates from Zhang et al.⁵ 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 2015¹⁰) 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 ± 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.,⁵⁰). A new estimate for total anthropogenic releases from
315 point sources to freshwaters, of 0.6kt/yr¹⁰, is included based on recent literature.^{7,49} An estimate for oil
316 and gas releases to marine systems (0.015 kt/yr¹⁰) 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 (^{3,5,7}). Kocman et al.'s ⁴⁹ compilation and evaluation of
321 global freshwater Hg contamination suggested that Liu et al.'s ⁴⁸ 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. ⁴⁹ advocated for a relatively low global riverine flux value similar to
324 that of Sunderland and Mason ⁵¹. 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. ⁵² 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. ⁵³ 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. ⁵² 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. ^{5,7,13,20} 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. ^{4,11,51,53-57} Since then, Amos et al. ¹³ 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.'s⁵ suggestion that the high emissions scenario is too high.

346 Even with the lower mining emissions scenario, Zhang et al.'s⁵ 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.⁵ is in good agreement with another recent estimate (58 ± 16 kt²⁰) derived using a different
351 methodology based on seawater Hg concentration profiles combined with anthropogenic CO₂ 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.¹¹ estimate of 53 kt used in AMAP/UNEP¹ (see Table 1).

356 Based on this revised global budget, the Hg budget in the world's oceans, as represented in Zhang et al.⁵
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.⁵ 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., see³⁸). 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^{1,5} or substantially
369 less.¹³ 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.⁵⁸⁻⁶³ 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.^{59, 60, 64}

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.⁵ brought their modelled emission and deposition history closer to the world-
380 wide lake sediment pattern (compared with the Streets et al.^{4,12} emission inventories and atmospheric
381 concentration calculations). However, the distinct bulge in modeled deposition during the late 19th and
382 early 20th 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 biota³³ 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's²⁷ 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.⁵ and
389 Streets et al.¹² 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.^{5, 7, 11, 20} But according to Selin⁶⁵ and Engstrom
401 et al.²², 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.⁶⁶

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.^{22, 65, 66}

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.^{5, 9, 13, 20, 22, 67-70} 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^{11, 51}. 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 determinations⁷¹). Past intercalibration exercises for seawater have only addressed total Hg, and the
438 results have indicated significant discrepancies among the participating laboratories.⁷² 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)⁷³⁻⁷⁷,
448 with a recent summation of the literature estimating 76 ± 30 t/yr from quiescent volcanic degassing, not
449 including effusions or eruptions.⁷⁷ For oceans, the AMAP/UNEP report¹ 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^{78, 79} 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.⁸⁰ 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.⁸¹ 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.⁸² Several recent papers indicate that SGD inputs of Hg may be locally as important
458 as atmospheric inputs, at least in some coastal environments.⁸³⁻⁸⁷ Additionally, the recent findings of
459 Zaferani et al.³⁸ 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.⁶² 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.⁵², 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.⁸⁸ 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.⁴² 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.⁸⁹ 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.^{7, 54, 90, 91} 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/UNEP¹, 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.^{22, 69} Zhang et al.⁶⁹ 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/UNEP¹, but this finding has been disputed.^{22, 69} 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

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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>.

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

	Mason et al. ¹¹ ; AMAP/UNEP ¹	Amos et al. ¹³	Zhang et al. ⁵	Lamborg et al. ²⁰	Present study ^b
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) ^c	58±16 ^d	55
Natural	305	122	191	258 ^e	258

767 ^a 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'¹³; prior to 1450 AD^{5, 18} which preceded New World Ag, Au and Hg production; and
769 about 1840 AD²⁰ 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.¹¹ and Lamborg et al.²⁰ 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. ^b estimates for this assessment modified
772 from Zhang et al.⁵ as described in text, and thus the anthropogenic values represent the impact of human activities since 1450 AD. ^c uncertainty
773 range shown in brackets. ^d based on an oceanic anthropogenic Hg:anthropogenic CO₂ ratio for 1994; a more recent (higher) oceanic CO₂
774 estimate gave an anthropogenic Hg estimate of 76 kt Hg.²⁰ ^e calculated by subtraction. n/a = not available.

Figure Captions

Figure 1. Glacial ice core records of atmospheric Hg deposition from (a) Mount Logan, Yukon⁴⁰, (b) Mount Geladaindong, Tibetan Plateau, China⁴², and (c) the NEEM site, Greenland⁴¹, compared with (d) the global atmospheric emission history since 1850 AD.¹² 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.⁵, based on the revised global budget shown in Fig. 2. Natural fluxes and masses in black, anthropogenic in red).







