Historical Mercury Releases from Commercial Products: Global Environmental Implications

1   **Historical mercury releases from commercial products: global environmental implications**

2   Hannah M. Horowitz,[†,*] Daniel J. Jacob,[†,‡] Helen M. Amos,[†] David G. Streets,[§] and Elsie M.

3   Sunderland[‡,∥]

4

5   [†]**Harvard University, Department of Earth and Planetary Sciences, Cambridge, MA, USA**

6   [‡]**School of Engineering and Applied Science, Harvard University, Cambridge, MA, USA**

7   [§]**Decision and Information Sciences Division, Argonne National Laboratory, Argonne, IL,**

8   **USA**

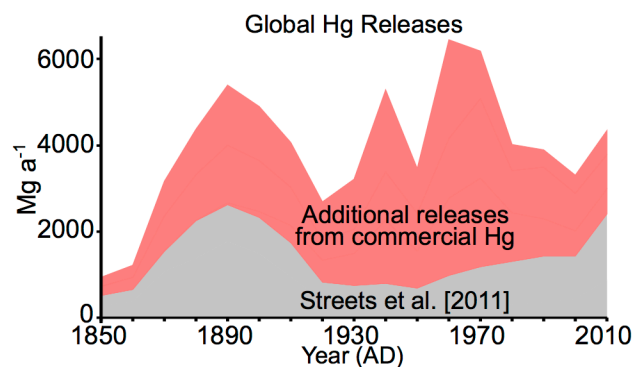9   [∥]**Department of Environmental Health, Harvard School of Public Health, Boston, MA, USA**

10

15

Global Hg Releases

16

ABSTRACT

Use and disposal of commercial products has contributed a large and previously unquantified anthropogenic source of mercury (Hg) to the global environment over the industrial era, with major implications for Hg accumulation in environmental reservoirs. We present a global inventory of commercial Hg uses and releases to the atmosphere, water, soil, and landfills from 1850 to 2010. Previous inventories of anthropogenic Hg releases have focused almost exclusively on atmospheric emissions. Cumulative anthropogenic Hg emissions since 1850 have recently been estimated at 220 Gg. We find that commercial use of Hg released an additional 540 Gg to the global environment since 1850 (20% to air, 30% to water, 30% to soil, 20% to landfills). Some of this release has been sequestered in landfills and benthic sediments, but 310 Gg actively cycles among geochemical reservoirs and contributes to elevated present-day environmental Hg concentrations. Commercial Hg use peaked in 1970 and has declined sharply since. Using our inventory to force a global biogeochemical model improves model consistency with observed (1) changes in atmospheric deposition recorded in many remote lake sediments and ombrotrophic peat bogs over the industrial era, and (2) declines in atmospheric Hg concentrations since the 1990s.

INTRODUCTION

34   Methylmercury, a toxin formed from inorganic Hg, bioaccumulates in aquatic food

35   chains and adversely affects human health on a global scale through fish consumption.[1,2] Hg has

36   been mined since antiquity and extensively used in many commercial products,[3] leading to its

37   eventual release to the environment upon disposal. Hg cycles rapidly between air, water, and soil

38   reservoirs so that releases to any of these reservoirs can contribute to oceanic Hg levels.[4]

39   Background levels of Hg in the environment have increased ~3 fold since pre-industrial times[5]

40   and may be 5 – 10 times above natural levels.[4,6] This has been conventionally attributed to

41   atmospheric emissions from mining and combustion.[7,8] Here we show that releases of

42   commercial Hg to air, water, and soil have contributed a large, previously unquantified source of

43   Hg to the global environment over the industrial era, with major implications for historical and

44   present-day conditions.

45   Hg is transferred from its stable lithospheric reservoir to surface environmental reservoirs

46   by natural geological processes, fossil fuel combustion, and mining (including for commercial

47   products). It then is exchanged between the atmosphere, surface ocean, and terrestrial

48   ecosystems on time scales of years to decades.[4] The atmospheric lifetime of gaseous elemental

49   Hg is of the order of a year, allowing transport and deposition on a global scale.[9] Hg is

50   eventually transferred to long-lived soil and deep-ocean pools over hundreds of years, and

51   returns to the lithosphere to close the cycle on a timescale of thousands of years.[10] The lasting

52   environmental legacy of Hg released to surface reservoirs mandates a historical perspective for

53   understanding present-day environmental burdens and for evaluating the effectiveness of

54   regulatory actions such as the Minamata Convention.[11]

55   While an estimated 215 Gg of Hg have been emitted directly to the atmosphere since

56   1850 from fuel combustion, metals smelting, mining, and chlor-alkali plants, an additional 616

57   Gg have been mined during the same period for numerous commercial uses.[12] These include

58   Hg-containing products (e.g. batteries) and manufacturing processes that involve Hg (e.g. vinyl

59   chloride monomer production). Commercial Hg enters the environment either during use or

60   following product disposal. Previous studies have estimated present-day environmental releases

61   of Hg from commercial products and processes only for a subset of uses and fate pathways, with

62   a predominant focus on atmospheric emissions.[13-23] The environmental fate of most of the mined

63   Hg has not yet been quantified.

64   Commercial Hg can enter the environment by various pathways. For example, Hg in

65   paint rapidly volatilizes to the atmosphere.[24] The chemical manufacturing industry historically

66   discharged large amounts of Hg directly into waterways, reflected by legacy contamination in

67   many estuaries today.[25-28] Hg-containing agricultural fungicides and pesticides were applied to

68   soil in large quantities for much of the 20th century.[29] Discarded Hg-containing batteries have

69   generally been incinerated or landfilled.[30, 31] More recently, many industries have made progress

70   toward recycling Hg in commercial products or phasing out its use.[32]

71   Here we quantify the global time-dependent historical releases of commercial Hg to

72   different environmental reservoirs (air, water, soil, landfills), and include these in a global

73   biogeochemical model[4] to investigate their impact on historical and present-day global Hg

74   accumulation. Water releases include effluent discharges to both estuaries and inland freshwater

75   systems, and soil releases are deposited to land or vegetation. Previous work has had difficulty

76   reconciling the temporal trend of anthropogenic emissions with archival records of historical

77   atmospheric Hg deposition, many of which show a peak in the 1970s.[33-36] Atmospheric

78   observations indicate a ~20% to 50% decrease in total gaseous mercury in the Northern

79   Hemisphere since 1995,[37, 38] at odds with atmospheric emission inventories that estimate

80   increased or flat emissions over this period.[12, 20] Soerensen et al.[38] suggested that the observed

81   atmospheric trend could be explained by declining oceanic evasion to the atmosphere due to

82   decreased seawater concentrations. Commercial use of Hg peaked in the 1970s and has declined

83   dramatically since,[12, 39] and we investigate how the related changes in historical commercial Hg

84   releases may play a role in reconciling these trends.

85   **METHODS**

86   We present a global, historical analysis tracking Hg from when it is mined, through all

87   known intentional uses and fate pathways, to its final time-dependent releases to different

88   environmental reservoirs. Commercial Hg uses are grouped by similar environmental release

89   patterns for a total of 14 use categories (Table 1). We estimate global environmental releases of

90   Hg and track recycled and landfilled quantities from each use category on a decadal scale

91   between 1850 and 2010. We first estimate the quantity of Hg consumed in each use category

92   constrained by the total amount of Hg mined globally. We then apply a series of distribution

93   factors that vary temporally and by economic development status of different countries to

94   distribute commercial Hg to its final environmental releases following a simplified substance

95   flow analysis (e.g. Barr Engineering[14]). Finally, we investigate the impacts of these global, time-

96   dependent releases on accumulation and cycling among environmental reservoirs using a seven-

97   box biogeochemical Hg model.

98   *Global Commercial Hg Consumption Patterns, 1850 – 2010*

99   We assume that significant Hg release from non-mining commercial Hg uses began in

100   1850. Anthropogenic releases prior to 1850 were mainly from mining.[12] Overall decadal

101   estimates of the magnitude of Hg used throughout the industrial era are constrained by global Hg

102 production from mining between 1850 and 1980[12, 39] combined with changes in the Hg supply

103 available for consumption due to government stockpiling[40] (Figure 1). We assume that mined Hg

104 that is not stockpiled is incorporated into products within a decade. Secondary Hg sources

105 (releases from strategic stockpiles, recovery from mining and smelting, and recycling of Hg-

106 containing products) became significant after 1980.[13, 32, 41] Therefore, for 1990 – 2010, we use

107 total Hg consumption from Wilson et al.[20] which includes both primary mining and secondary

108 sources.

109   We then partition the global total Hg supply into individual uses. Methods used to

110 estimate Hg consumption for each category vary depending on data availability. We divide

111 countries into two groups, developed countries (North America, OECD/EU Europe, Oceania)

112 and developing countries including economies in transition (rest of world), based on similarities

113 in environmental regulations and control technologies within each group that lead to differences

114 in Hg use and release patterns between them. Data from Streets et al.[12] are used to constrain total

115 Hg consumed globally for the chlor-alkali industry between 1850 and 1930 and silver and gold

116 mining between 1850 and 1990, including artisanal and small-scale gold mining (ASGM).

117 Decadal use patterns available for the United States[42, 43] are used to estimate global consumption

118 of Hg in the remaining uses for 1850 – 1960. During this period, the US consumed ~25% of total

119 Hg mined globally and its Hg use data is the most complete.

120   The ca. 1970 onset of environmental regulations targeting Hg releases in developed

121 countries resulted in major changes in Hg consumption patterns.[25] We therefore estimate Hg

122 consumption separately for developing countries from 1970 on. For 1970 and 1980, we divide

123 the global total Hg supply between the developed and developing world by the fraction of global

124 GDP held by each group of countries.[44] Consumption patterns for the developed world are

125   assumed to follow those of the US in 1970 and 1980.[45] Consumption patterns for the developing

126   world in 1970 and 1980 are assumed to be similar to those of the US in 1960, when Hg use was

127   unregulated. For 1990 – 2000, we use regionally resolved Hg consumption data from Wilson et

128   al.[20] For 2010, we use annual consumption data from AMAP/UNEP[22] for the uses available, and

129   extrapolate the 2000 – 2005 trend from Wilson et al.[20] for the remaining uses.

130   *Environmental Releases of Commercial Hg*

131   Figure 2 shows a generic substance flow analysis diagram that tracks the fate of

132   commercial Hg for each decade and use category (Table 1) to its eventual release in different

133   environmental reservoirs. First, the Hg consumed in each use category is divided among direct

134   releases to air, water, and soil, recycling, and disposal to solid waste or wastewater treatment

135   ('Tier 1' distribution factors). Certain use categories have additional disposal pathways with

136   environmental fates that are distinct from general solid waste or wastewater disposal. Hg

137   entering the three waste disposal pathways is divided further ('Tier 2' distribution factors). Solid

138   waste is split between disposal in landfills, incineration, and direct disposal to soil, wastewater is

139   partially captured in sewage sludge and the rest is released to water, and 'Other Disposal' is

140   distributed between air, land, and landfills. A third tier of distribution factors is needed to

141   characterize environmental releases for solid waste incineration (emitted to air, or captured in ash

142   and then deposited to soil or in landfills) and sewage sludge (incinerated and emitted to air,

143   applied to soil, or disposed of in landfills). Dental amalgam has unique fate pathways not

144   represented in Figure 2. Some Hg in teeth is permanently stored during burial[46] or partially

145   released to air, water, and soil upon cremation.

146   Distribution factors for each use category were estimated from a variety of sources

147   (Tables S1 and S2). Distribution factors are applied globally for 1850 – 1960, and separately for

148   the developed and developing world between 1970 and 2010. We use previous decadal estimates

149   from Streets et al.[12] for global atmospheric emissions from chlor-alkali plants, silver and large-

150   scale gold mining, and ASGM, except for 2010 ASGM emissions for which we use

151   AMAP/UNEP[22] estimates.

152   Temporal variability in distribution factors is governed by the availability of evidence

153   that releases have changed from one decade to another due to regulatory controls and other

154   factors. Global distribution factors are held constant in time through 1950, with variation in 1960

155   for three use categories (VCM and Other Chemical, Paint, and Pesticides and Fertilizer). This

156   reflects significant changes in consumption patterns (a change from chemicals to laboratory uses,

157   marine anti-fouling paint to home interior/exterior latex paint, and agricultural to pulp and paper

158   fungicides, respectively). Different distribution factors in the developed world are applied for

159   each decade between 1970 and 2010. Developing world distribution factors are assumed constant

160   for 1970 – 2010. The "Other" category in Table 1 (9% of 1850 – 2010 global consumption)

161   encompasses a diverse set of uses with an unknown distribution, and we assume for this category

162   the average fate of all other categories.

163   Releases to different environmental reservoirs are calculated on a global scale by

164   multiplying the Hg consumed in each use category and decade by the corresponding distribution

165   factors. Most products are disposed of and enter the environment within the decade when they

166   were produced, and manufacturing processes generally consume and release Hg within a year.[13,

167   15, 16, 30, 47-50] Products in the Wiring Devices and Industrial Measuring Devices category are often

168   in use for 20-50 years before disposal.[13-15, 30, 49] For these products we follow the methods of

169   Jasinski et al.[13] and Cain et al.[16] and assume that 10% are discarded after 10 years, 40% after 30

170   years, and the remaining 50% after 50 years. Dental amalgams generally remain in living teeth

171   for 10 to 30 years or more. We estimate excretion and exhalation releases from dental amalgam

172   to air and water during this time and track the remaining Hg that will be released through

173   cremation pathways or permanently stored through burial after 30 to 50 years, depending on

174   average life expectancy[51] and ages of individuals receiving fillings.[16]

175   Recycled Hg is estimated separately for internal reuse of Hg in chemicals manufacturing

176   and large-scale mining[30, 52, 53] and external recycling of Hg in products like batteries that returns

177   Hg to the global Hg supply for future use.[53] External recycling did not become widespread until

178   1990.[13] We do not tie our estimates of recycled Hg to global Hg supply, and instead use

179   estimated total Hg supply from Wilson et al.[20] which includes all secondary sources for 1990 –

180   present. We assume that no Hg is released to the environment during the recycling process,

181   based on available data suggesting releases are negligible.[53]

182   *Implications for the Biogeochemical Hg Cycle and Atmospheric Trends*

183   We use the fully-coupled global biogeochemical Hg box model from Amos et al.[4] to

184   track the fate of commercial Hg after it has been released to the environment. The model

185   includes seven reservoirs that represent the atmosphere, ocean (surface, subsurface, and deep),

186   and terrestrial pools (fast, slow, and armored). Fluxes between reservoirs are determined by first-

187   order rate coefficients applied to the inventory of the exporting reservoir. Atmospheric rate

188   coefficients are from Holmes et al.[54] and oceanic rate coefficients are from Soerensen et al.[55] and

189   Sunderland and Mason[56] (for a full list, see Table S3). Riverine rate coefficients have been

190   updated following Amos et al.[57] to include the settling of particle-bound Hg to benthic estuarine

191 and shelf sediments. This effectively adds a permanent sink from the terrestrial pools. Primary

192 anthropogenic and geogenic emissions are treated as external forcings.

193 We added a landfill reservoir to this model. Landfills can emit Hg into the atmosphere

194 through vent pipes, diffusion from cover soil, and from the "working face" where waste is

195 exposed and actively dumped.[31] They can also release Hg into groundwater and soils through the

196 base of the landfill but this appears to be negligible.[58] Data available on Hg emissions for

197 managed landfills in China,[31] the United States,[59] and Korea[60] indicate low values. We find a

198 mean lifetime of 20,000 years for Hg in landfills by combining emissions values for each site

199 with estimated Hg reservoirs inferred from the waste content and disposal magnitudes. Landfills

200 as defined here can therefore effectively be viewed as a permanent sink.

201 Commercial Hg enters the biogeochemical cycle via the atmosphere, water, soil, and

202 landfills. Hg releases to soil are distributed among the three terrestrial reservoirs of the model in

203 the same manner as atmospherically deposited Hg in Amos et al.[4] Hg releases to water are

204 distributed as 90% to inland freshwater systems and 10% to estuaries based on the distribution of

205 present-day point sources.[57, 61] We assume that 75% of the Hg input to inland freshwater systems

206 is sequestered permanently in sediments and 25% evades to the atmosphere, based on models for

207 a variety of lakes and rivers.[62] Based on previous work, we assume that 50% of the Hg directly

208 released to estuaries is transported to the surface ocean, 10% evades to the atmosphere, and 40%

209 is sequestered permanently in coastal sediments.[63, 64] In this manner, we estimate that 70% of Hg

210 released to water is permanently sequestered, 23% enters the atmosphere, and 7% enters the

211 surface ocean.

212 We apply the box model to time-dependent simulations from 2000 BC to 2010 following

213 the methods described in Amos et al.[4] We simulate 1850 – 2010 with anthropogenic atmospheric

214 emissions from Streets et al.[12] plus the releases from commercial Hg quantified in this study. We

215 evaluate the model with three global observational constraints, following Amos et al.[4]: (1) the

216 present-day atmospheric inventory (best estimate of 5000 Mg, range 4600 – 5600 Mg), (2) the

217 present-day mean upper (0 to 1500 m) ocean concentration (best estimate of 1.0 pM, range 0.5-

218 1.5 pM), and (3) the relative anthropogenic enrichment factor (AEF) in atmospheric deposition

219 between pre-industrial and present-day (best estimate of 3, range 2 to 5). We define our model

220 AEF as the ratio of average 1985-2000 deposition to average 1760-1880 deposition.[65, 66] These

221 two time intervals are empirically determined from the compilation of lake sediments described

222 in Biester et al.[67] to provide a more consistent comparison between models and observations.[65]

223 **RESULTS AND DISCUSSION**

224 *Global Commercial Hg Consumption Patterns, 1850 – 2010*

225   Figure 3 shows the global commercial use of Hg since 1850 for all categories described

226 in Table 1, and partitioned between the developed and developing world after 1970. Prior to

227 1900, almost all mined Hg was used in silver and gold mining. In the 20th century, Hg uses

228 diversified greatly. Hg use in large-scale mining declined following the end of the gold rush and

229 as extraction methods that did not require Hg became widespread. The 1940s peak in Figure 3 is

230 driven by chemicals production for munitions during WWII. The 1970s peak represents the

231 height of Hg use in consumer products like paint and batteries. Total consumption declined after

232 the 1970s when many developed countries implemented regulations on Hg uses and

233 environmental releases. Since 1990, the developing world has dominated global Hg

234 consumption. ASGM in developing countries is presently the largest use of Hg globally, and is

235 increasing.[22, 68]

Environmental Releases of Commercial Hg

237   Figure 4 compares the historical atmospheric emissions inventory of Streets et al.[12]

238 (including sources from combustion, metals smelting, mining, and chlor-alkali plants) with our

239 best estimate of additional releases to air, water, soil, and landfills from commercial Hg. Streets

240 et al.[12] estimate total emissions to air of 215 Gg since 1850. Additional releases in our inventory

241 over the same period total 540 Gg. Of these, 230 Gg are permanently sequestered in landfills or

242 in benthic sediments of freshwater and estuarine systems. The remaining 310 Gg (including 110

243 Gg emitted to air) cycle between biogeochemical reservoirs and represent a larger anthropogenic

244 perturbation to the global Hg cycle than the 215 Gg of Streets et al.[12] Commercial Hg thus

245 represents a major, previously unquantified source of Hg to the global environment. The

246 temporal pattern of anthropogenic Hg releases is also affected. Whereas Streets et al.[12] indicate

247 rising emissions since 1950, our estimate shows a decline in total releases from 1970 to 2000.

248   Figure 5 presents the historical contributions of individual commercial use categories to

249 global environmental releases to air, water, soil, and landfills. Releases to air, water, and soil all

250 show similar enhancements from late 19th-century mining. Differences are attributable to

251 changes in the fate of commercial Hg over time. Emissions to air peak in 1970, mainly due to

252 paint volatilization and incineration of batteries. Although Hg use in batteries increased from

253 1970 to 1980, open-air waste burning at landfills was eliminated during this period following

254 solid waste regulations.[69, 70] Use of explosives and weapons was a major emitter to air during

255 1900 – 1950 with a peak in WWII.

256   Water releases also exhibit a peak during WWII, due to laboratory uses and chemicals

257   manufacturing. The overall maximum occurs in 1960, with a steep subsequent decline following

258   implementation of chlor-alkali liquid effluent regulations in the early 1970s in North America

259   and Europe.[71, 72] Implementation of wastewater treatment from the 1980s onward led to even

260   greater declines in water releases,[73] but contributes a small amount to soils due to application of

261   Hg-containing sludges.[16, 53] Similarly, chlor-alkali plants began capturing Hg in sludges in the

262   1970s, which were subsequently dumped on land or landfilled on-site.[72] The 1970 peak in soil

263   releases is driven by Hg used in chlor-alkali plants and Hg-containing pesticides and fertilizer

264   that were applied directly to land.

265   *Implications for the Biogeochemical Hg Cycle and Atmospheric Trends*

266   Figure 6 shows simulated atmospheric Hg from 1850-present after adding our inventory

267   of commercial Hg releases to the updated global biogeochemical Hg model, which includes

268   burial of riverine Hg in benthic sediments of coastal marine systems from Amos et al.[57] and an

269   additional reservoir representing landfills. Our simulated present-day atmospheric reservoir is

270   5800 Mg, the mean Hg concentration in the upper ocean is 1.5 pM, and the AEF for atmospheric

271   deposition is 4.4. The original Amos et al.[4] simulation not including commercial Hg yielded a

272   present-day atmosphere of 5300 Mg, but did not account for burial of riverine Hg. Accounting

273   for burial without commercial Hg results in an atmosphere that is too low (2700 Mg).

274   Conversely, including commercial Hg in the original Amos et al.[4] simulation without burial

275   would yield a present-day atmospheric reservoir of 10,000 Mg, much higher than observed.

276   Our simulated present-day atmospheric reservoir of 5800 Mg is still slightly higher than

277   the observational range (4600-5600 Mg). This is due to the increase over the past decade (Figure

278 6) driven by rising anthropogenic atmospheric emissions in the Streets et al.[12] inventory

279 (primarily from coal burning in Asia) and rising releases from ASGM[22] (Figures 3 and 4).

280 However, Wilson et al.[20] suggest that global anthropogenic emissions have in fact remained

281 relatively constant since 2000, and AMAP/UNEP[22] suggest that the ASGM increase since 2000

282 may be an artifact of improved reporting. We conducted a sensitivity simulation holding constant

283 anthropogenic atmospheric emissions and ASGM releases for the 2000-2010 period, and results

284 are shown as the dashed line in Figure 6. We obtain in that simulation an atmospheric reservoir

285 of 5000 Mg, more consistent with observations, and unchanged upper ocean concentration of 1.5

286 pM and AEF of 4.4. Alternatively, the atmospheric reservoir could be reduced within the range

287 of observational constraints if the efficacy of Hg re-emission from soils were decreased, a

288 change supported by recent observational evidence.[74, 75]

289 Inclusion of commercial Hg releases in our global biogeochemical model improves

290 model consistency with archival records of atmospheric deposition. Lake sediments and

291 ombrotrophic peat bogs generally indicate a gradual rise over the industrial era with a peak in the

292 1970s.[33-36] Figure 6 indicates a 1970s peak in simulated atmospheric Hg and a muted 19th

293 century mining signal. Without the inclusion of commercial Hg, model deposition increases from

294 1970 to present and there is a prominent 19th century peak.[4] Our inventory also helps to explain

295 the observed 1990-present declines in atmospheric Hg over North America and Europe.[37, 38]

296 Our work shows that environmental releases of commercial Hg to air, water, and soil

297 over the industrial period have represented a major and previously unquantified perturbation to

298 Hg in the global environment. The legacy of this source in oceanic and terrestrial reservoirs has

299 important implications for policy. Future work should examine the geographical distribution of

300 commercial Hg releases and its impact on regional-scale environmental Hg loadings and

atmospheric trends. Better understanding of the role of soils for long-term storage of

anthropogenic Hg is also critically needed.

SUPPORTING INFORMATION. Additional information on data sources used to estimate

distribution factors (Table S1), distribution factors used in this study (Table S2), and model rate

coefficients (Table S3). This material is available free of charge via the Internet at

http://pubs.acs.org.

REFERENCES

1.   Mahaffey, K. R.; Sunderland, E. M.; Chan, H. M.; Choi, A. L.; Grandjean, P.; Marien,

K.; Oken, E.; Sakamoto, M.; Schoeny, R.; Weihe, P.; Yan, C. H.; Yasutake, A. Balancing the

benefits of n-3 polyunsaturated fatty acids and the risks of methylmercury exposure from fish

consumption. *Nutrition Reviews* **2011,** *69*, (9), 493-508.

2.   Karagas, M. R.; Choi, A. L.; Oken, E.; Horvat, M.; Schoeny, R.; Kamai, E.; Cowell, W.;

Grandjean, P.; Korrick, S. Evidence on the Human Health Effects of Low-Level Methylmercury

Exposure. *Environmental Health Perspectives* **2012,** *120*, (6), 799-806.

3.   Nriagu, J. O. Production and uses of mercury. In *The biogeochemistry of mercury in the

environment;* Nriagu, J. O. Ed.; Elsevier/North-Holland Biomedial Press: Amsterdam, the

Netherlands, 1979; pp 23-40.

321   4.   Amos, H. M.; Jacob, D. J.; Streets, D. G.; Sunderland, E. M. Legacy impacts of all-time

322   anthropogenic emissions on the global mercury cycle. *Global Biogeochemical Cycles* **2013,** *27*,

323   (2), 410-421.

324   5.   Fitzgerald, W. F.; Engstrom, D. R.; Mason, R. P.; Nater, E. A. The case for atmospheric

325   mercury contamination in remote areas. *Environmental Science & Technology* **1998,** *32*, (1), 1-7.

326   6.   Serrano, O.; Martinez-Cortizas, A.; Mateo, M. A.; Biester, H.; Bindler, R. Millennial

327   scale impact on the marine biogeochemical cycle of mercury from early mining on the Iberian

328   Peninsula. *Global Biogeochemical Cycles* **2013,** *27*, (1), 21-30.

329   7.   Mason, R. P.; Fitzgerald, W. F.; Morel, F. M. M. The Biogeochemical Cycling of

330   Elemental Mercury - Anthropogenic Influences. *Geochim. Cosmochim. Acta* **1994,** *58*, (15),

331   3191-3198.

332   8.   Selin, N. E.; Jacob, D. J.; Yantosca, R. M.; Strode, S.; Jaegle, L.; Sunderland, E. M.

333   Global 3-D land-ocean-atmosphere model for mercury: Present-day versus preindustrial cycles

334   and anthropogenic enrichment factors for deposition. *Global Biogeochemical Cycles* **2008,** *22*,

335   (2).

336   9.   Slemr, F.; Schuster, G.; Seiler, W. Distribution, Speciation, and Budget of Atmospheric

337   Mercury. *J Atmos Chem* **1985,** *3*, (4), 407-434.

338   10.   Andren, M. O.; Nriagu, J. O. The global cycle of mercury. In *The biogeochemistry of*

339   *mercury in the environment*; Nriagu, J. O. Ed.; 1979; pp 1-15.

340   11.   *Minamata Convention on Mercury: Text and Annexes*; United Nations Environment

341   Programme: Nairobi, Kenya, 2013.

342   12.   Streets, D. G.; Devane, M. K.; Lu, Z.; Bond, T. C.; Sunderland, E. M.; Jacob, D. J. All-

343   Time Releases of Mercury to the Atmosphere from Human Activities. *Environmental Science &*

344   *Technology* **2011,** *45*, (24), 10485-10491.

345   13.   Jasinski, S. M. *The materials flow of mercury in the United States;* Bureau of Mines

346   Information Circular IC 9412; U.S. Department of the Interior: Washington, DC, 1994.

347   14.   *Substance Flow Analysis of Mercury in Products*; Barr Engineering: Minneapolis, MN,

348   August 15, 2001.

349   15.   *Assessment of Mercury Releases from the Russian Federation*; Arctic Council Action

350   Plan to Eliminate Pollution of the Arctic (ACAP), Russian Federal Service for Environmental,

351   Technological and Atomic Supervision & Danish Environmental Protection Agency:

352   Copenhagen, Denmark, 2005.

353   16.   Cain, A.; Disch, S.; Twaroski, C.; Reindl, J.; Case, C. R. Substance flow analysis of

354   mercury intentionally used in products in the United States. *Journal of Industrial Ecology* **2007,**

355   *11*, (3), 61-75.

356   17.   Kindbom, K.; Munthe, J. *Product-related emissions of Mercury to Air in the European*

357   *Union*; IVL Swedish Environmental Research Institute Ltd. : Göteborg, Sweden, 2007.

358   18.   Pacyna, E. G.; Pacyna, J. M.; Sundseth, K.; Munthe, J.; Kindbom, K.; Wilson, S.;

359   Steenhuisen, F.; Maxson, P. Global emission of mercury to the atmosphere from anthropogenic

360   sources in 2005 and projections to 2020. *Atmospheric Environment* **2010,** *44*, (20), 2487-2499.

361   19.   Pirrone, N.; Cinnirella, S.; Feng, X.; Finkelman, R. B.; Friedli, H. R.; Leaner, J.; Mason,

362   R.; Mukherjee, A. B.; Stracher, G. B.; Streets, D. G.; Telmer, K. Global mercury emissions to the

363   atmosphere from anthropogenic and natural sources. *Atmospheric Chemistry and Physics* **2010,**

364   *10,* (13), 5951-5964.

365   20.   Wilson, S.; Munthe, J.; Sundseth, K.; Kindbom, K.; Maxson, P.; Pacyna, J. M.;

366   Steenhuisen, F. *Updating Historical Global Inventories of Anthropogenic Mercury Emissions to*

367   *Air*; Arctic Monitoring and Assessment Program (AMAP): Oslo, Norway, 2010.

368   21.   Sundseth, K.; Pacyna, J.; Pacyna, E.; Panasiuk, D. Substance Flow Analysis of Mercury

369   Affecting Water Quality in the European Union. *Water, Air, & Soil Pollution* **2011**, 1-14.

370   22.   *Technical Background Report for the Global Mercury Assessment 2013*; Arctic

371   Monitoring and Assessment Programme (AMAP), Oslo, Norway/UNEP Chemicals Branch,

372   Geneva, Switzerland: 2013.

373   23.   Chakraborty, L. B.; Qureshi, A.; Vadenbo, C.; Hellweg, S. Anthropogenic Mercury

374   Flows in India and Impacts of Emission Controls. *Environmental Science & Technology* **2013,**

375   *47,* (15), 8105-8113.

376   24.   Taylor, C. G. The loss of mercury from fungicidal paints. *Journal of Applied Chemistry*

377   **1965**, 232-236.

378   25.   D'Itri, P. A.; D'Itri, F. M. *Mercury Contamination: A Human Tragedy*; John Wiley &

379   Sons: New York, 1977.

380   26.   Rudd, J. W. M.; Turner, M. A.; Furutani, A.; Swick, A. L.; Townsend, B. E. The English

381   Wabigoon River System .1. A Synthesis of Recent Research with a View Towards Mercury

382   Amelioration. *Can J Fish Aquat Sci* **1983,** *40*, (12), 2206-2217.

383 27.   Gill, G. A.; Bloom, N. S.; Cappellino, S.; Driscoll, C. T.; Dobbs, C.; McShea, L.; Mason,

384 R.; Rudd, J. W. M. Sediment-water fluxes of mercury in Lavaca Bay, Texas. *Environmental*

385 *Science & Technology* **1999,** *33*, (5), 663-669.

386 28.   Kocman, D.; Horvat, M.; Pirrone, N.; Cinnirella, S. Contribution of contaminated sites to

387 the global mercury budget. *Environmental Research* **2013,** *125*, 160-170.

388 29.   Rissanen, K.; Miettinen, J. K. Use of mercury compounds in agriculture and its

389 implications. In *Mercury Contamination in Man and his Environment: a joint undertaking by the*

390 *International Labor Organisation, Food and Agriculture Organization of the United Nations,*

391 *The World Health Organization and the International Atomic Energy Agency*; International

392 Atomic Energy Agency: Vienna, Austria, 1972.

393 30.   *Characterization of Products Containing Mercury in Muncipal Solid Waste in the United*

394 *States, 1970 to 2000*; U.S. Environmental Protection Agency, Office of Solid Waste, Municipal

395 and Industrial Solid Waste Division: Washington, DC, 1992.

396 31.   Li, Z. G.; Feng, X.; Li, P.; Liang, L.; Tang, S. L.; Wang, S. F.; Fu, X. W.; Qiu, G. L.;

397 Shang, L. H. Emissions of air-borne mercury from five municipal solid waste landfills in

398 Guiyang and Wuhan, China. *Atmospheric Chemistry and Physics* **2010,** *10*, (7), 3353-3364.

399 32.   Brooks, W. E.; Matos, G. R. Mercury recycling in the United States in 2000. In *Flow*

400 *studies for recycling metal commodities in the United States: U.S. Geological Survey Circular*

401 *1196-U*, Sibley, S. F. comp. Ed.; 2005; p 21.

402   33.   Kamman, N. C.; Engstrom, D. R. Historical and present fluxes of mercury to Vermont

403   and New Hampshire lakes inferred from Pb-210 dated sediment cores. *Atmospheric Environment*

404   **2002,** *36*, (10), 1599-1609.

405   34.   Engstrom, D. R.; Balogh, S. J.; Swain, E. B. History of mercury inputs to Minnesota

406   lakes: Influences of watershed disturbance and localized atmospheric deposition. *Limnol*

407   *Oceanogr* **2007,** *52*, (6), 2467-2483.

408   35.   Fain, X.; Ferrari, C. P.; Dommergue, A.; Albert, M. R.; Battle, M.; Severinghaus, J.;

409   Arnaud, L.; Barnola, J. M.; Cairns, W.; Barbante, C.; Boutron, C. Polar firn air reveals large-

410   scale impact of anthropogenic mercury emissions during the 1970s. *Proceedings of the National*

411   *Academy of Sciences of the United States of America* **2009,** *106*, (38), 16114-16119.

412   36.   Allan, M.; Le Roux, G.; Sonke, J. E.; Piotrowska, N.; Streel, M.; Fagel, N.

413   Reconstructing historical atmospheric mercury deposition in Western Europe using: Misten peat

414   bog cores, Belgium. *Science of the Total Environment* **2013,** *442*, 290-301.

415   37.   Slemr, F.; Brunke, E. G.; Ebinghaus, R.; Kuss, J. Worldwide trend of atmospheric

416   mercury since 1995. *Atmospheric Chemistry and Physics* **2011,** *11*, (10), 4779-4787.

417   38.   Soerensen, A. L.; Jacob, D. J.; Streets, D. G.; Witt, M. L. I.; Ebinghaus, R.; Mason, R. P.;

418   Andersson, M.; Sunderland, E. M. Multi-decadal decline of mercury in the North Atlantic

419   atmosphere explained by changing subsurface seawater concentrations. *Geophysical Research*

420   *Letters* **2012,** *39*.

421 39.   Hylander, L. D.; Meili, M. 500 years of mercury production: global annual inventory by

422 region until 2000 and associated emissions. *Science of the Total Environment* **2003,** *304*, (1-3),

423 13-27.

424 40.   Mercury statistics. In *Historical statistics for mineral and material commodities in the*

425 *United States: U.S. Geological Survey Data Series 140*, Kelly, T. D.; Matos, G. R. Comps.;

426 USGS: 2012, accessed September 25, 2013, at http://minerals.usgs.gov/ds/2005/140/.

427 41.   Maxson, P. *Mercury flows in Europe and the world: the impact of decommissioned chlor-*

428 *alkali plants*; Concorde East/West Sprl for the European Commission Environment Directorate-

429 General Brussels, Belgium, February, 2004.

430 42.   *Mineral Resources of the United States*. U.S. Geological Survey/Bureau of Mines, US

431 Department of the Interior, Government Printing Office: Washington, D.C. 1882 - 1929.

432 43.   *Minerals Yearbook*. US Bureau of Mines, US Department of the Interior, Government

433 Printing Office: Washington, D.C. USA, 1941 - 1968.

434 44.   GDP and its breakdown at constant 2005 prices in US dollars - All countries and

435 regions/subregions (totals) for all years. In *National Accounts Main Aggregates Database*,

436 United Nations Statistics Division: 2012.

437 45.   *Metal statistics*. American Metal Mart: New York, 1960 - 1995.

438 46.   Arenholt-Bindslev, D. Environmental aspects of dental filling materials. *Eur J Oral Sci*

439 **1998,** *106*, (2), 713-720.

440   47.   *Mercury Study Report to Congress Volume II: An Inventory of Anthropogenic Mercury*

441   *Emissions in the United States*; Office of Air Quality Planning & Standards and Office of

442   Research and Development, U.S. Environmental Protection Agency: December, 1997.

443   48.   Floyd, P.; Zarogiannis, P.; Crane, M.; Tarkowski, S.; Bencko, V. *Risks to health and the*

444   *environment related to the use of mercury products*; Risk & Policy Analysts for the European

445   Commission, DG Enterprise: Norfolk, UK, 2002.

446   49.   Hagreen, L. A.; Lourie, B. A. Canadian mercury inventories: the missing pieces.

447   *Environmental Research* **2004,** *95*, (3), 272-281.

448   50.   *Report on the major mercury-containing products and processes, their substitutes and*

449   *experience in switching to mercury-free products and processes*;

450   UNEP(DTIE)/Hg/OEWG.2/7/Add.1; United Nations Environment Programme (UNEP): Nairobi,

451   Kenya, 2008.

452   51.   *World Population Prospects: The 2010 Revision, Volume I: Comprehensive Tables*;

453   ST/ESA/SER.A/313; United Nations Department of Economic and Social Affairs Population

454   Division: New York, 2011.

455   52.   *NRDC submission to UNEP in response to March 2006 request for information on*

456   *mercury supply, demand, and trade*; National Resources Defense Council (NRDC): Washington,

457   DC, May, 2006.

458   53.   *Toolkit for Identification and Quantification of Mercury Sources, Reference Report and*

459   *Guidline for Inventory Level 2, Version 1.2, April 2013*; UNEP Chemicals Branch: Geneva,

460   Switzerland, 2013.

461 54.   Holmes, C. D.; Jacob, D. J.; Corbitt, E. S.; Mao, J.; Yang, X.; Talbot, R.; Slemr, F.

462 Global atmospheric model for mercury including oxidation by bromine atoms. *Atmospheric*

463 *Chemistry and Physics* **2010,** *10*, (24), 12037-12057.

464 55.   Soerensen, A. L.; Sunderland, E. M.; Holmes, C. D.; Jacob, D. J.; Yantosca, R. M.; Skov,

465 H.; Christensen, J. H.; Strode, S. A.; Mason, R. P. An Improved Global Model for Air-Sea

466 Exchange of Mercury: High Concentrations over the North Atlantic. *Environmental Science &*

467 *Technology* **2010,** *44*, (22), 8574-8580.

468 56.   Sunderland, E. M.; Mason, R. P. Human impacts on open ocean mercury concentrations.

469 *Global Biogeochemical Cycles* **2007,** *21*, (4).

470 57.   Amos, H. M.; Jacob, D. J.; Sunderland, E.; Horowitz, H. M.; et al. Impacts of recent

471 changes in mercury discharges from rivers on the marine environment. To be submitted for

472 publication.

473 58.   Li, Z.; Feng, X. Balance of Mercury in a Modern Municipal Solid Waste Landfill in

474 China. In *Air & Waste Management Association International Specialty Conference*, Xi'an,

475 China, 2010.

476 59.   Lindberg, S. E.; Southworth, G. R.; Bogle, M. A.; Blasing, T. J.; Owens, J.; Roy, K.;

477 Zhang, H.; Kuiken, T.; Price, J.; Reinhart, D.; Sfeir, H. Airborne emissions of mercury from

478 municipal solid waste. I: New measurements from six operating landfills in Florida. *Journal of*

479 *the Air & Waste Management Association* **2005,** *55*, (7), 859-869.

480 60.   Kim, S.; Karl, T.; Guenther, A.; Tyndall, G.; Orlando, J.; Harley, P.; Rasmussen, R.;

481 Apel, E. Emissions and ambient distributions of Biogenic Volatile Organic Compounds (BVOC)

482   in a ponderosa pine ecosystem: interpretation of PTR-MS mass spectra. *Atmospheric Chemistry*

483   *and Physics* **2010,** *10*, (4), 1759-1771.

484   61.   Kocman, D.; Horvat, M.; et al. A Global Inventory of Present-Day Mercury Releases to

485   Aquatic Environments. To be submitted for publication.

486   62.   Knightes, C. D.; Sunderland, E. M.; Barber, M. C.; Johnston, J. M.; Ambrose, R. B.

487   Application of Ecosystem-Scale Fate and Bioaccumulation Models to Predict Fish Mercury

488   Response Times to Changes in Atmospheric Deposition. *Environ Toxicol Chem* **2009,** *28*, (4),

489   881-893.

490   63.   Mason, R. P.; Lawson, N. M.; Lawrence, A. L.; Leaner, J. J.; Lee, J. G.; Sheu, G. R.

491   Mercury in the Chesapeake Bay. *Mar Chem* **1999,** *65*, (1-2), 77-96.

492   64.   Sunderland, E. M.; Dalziel, J.; Heyes, A.; Branfireun, B. A.; Krabbenhoft, D. P.; Gobas,

493   F. A. P. C. Response of a Macrotidal Estuary to Changes in Anthropogenic Mercury Loading

494   between 1850 and 2000. *Environmental Science & Technology* **2010,** *44*, (5), 1698-1704.

495   65.   Sonke, J. E. GET-Observatoire Midi-Pyrénées, CNRS, Université de Toulouse III,

496   Toulouse, France. Personal communication, 2014.

497   66.   Amos, H. M.; Sunderland, E.; Corbitt, E. S.; Hedgecock, I.; Kocman, D.; Krabbenhoft,

498   D.; Lamborg, C. H.; Obrist, D.; Pirrone, N.; Sonke, J. E.; Witt, M. L. I.; Horowitz, H. M.

499   Defining natural and anthropogenic mercury impacts. To be submitted for publication.

500   67.   Biester, H.; Bindler, R.; Martinez-Cortizas, A.; Engstrom, D. R. Modeling the past

501   atmospheric deposition of mercury using natural archives. *Environmental Science & Technology*

502   **2007,** *41*, (14), 4851-4860.

503   68.   Telmer, K. M.; Veiga, M. M. World Emissions of Mercury from Artisanal and Small

504   Scale Gold Mining. *Mercury Fate and Transport in the Global Atmosphere* **2009**, 131-172.

505   69.   *Municipal Solid Waste in the United States: 2001 Facts and Figures*; EPA530-R-03-011;

506   U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response:

507   Washington, DC, 2003.

508   70.   *Modern Landfills: A Far Cry from the Past*; National Solid Wastes Management

509   Association: Washington, DC, 2008.

510   71.   Flewelling, F. J. In *Loss of mercury to the environment from chlor-alkali plants*, Special

511   symposium on mercury in man's environment, Ottawa, Canada, February 15-16, 1971; Watkin,

512   J. E., Ed.; National Research Council of Canada: Ottawa, Canada, 1971.

513   72.   Trip, L.; Thorleifson, M. *The Canadian Mercury Cell Chlor-Alkali industry: Mercury*

514   *Emissions and Status of Facilities 1935 - 1996*; Environment Canada, Transboundary Air Issues

515   Branch: Quebec, Canada, April, 1998.

516   73.   *Materials balance and technology assessment of mercury and its compounds on national*

517   *and regional bases*; EPA 560/3-75-007; U.S. Environmental Protection Agency Office of Toxic

518   Substances: Washington, D.C. October, 1975.

519   74.   Obrist, D.; Pokharel, A. K.; Moore, C. Vertical Profile Measurements of Soil Air Suggest

520   Immobilization of Gaseous Elemental Mercury in Mineral Soil. *Environmental Science &*

521   *Technology* **2014,** *48*, (4), 2242-2252.

522   75.   Krabbenhoft, D. Understanding the Propagation of Atmospheric Mercury through

523   Terrestrial Landscapes: After Twenty Five Years of Research does the Story Make Sense?

524   Presented at 11th International Conference on Mercury as a Global Pollutant, Edinburgh,

525   Scotland, July 2013.
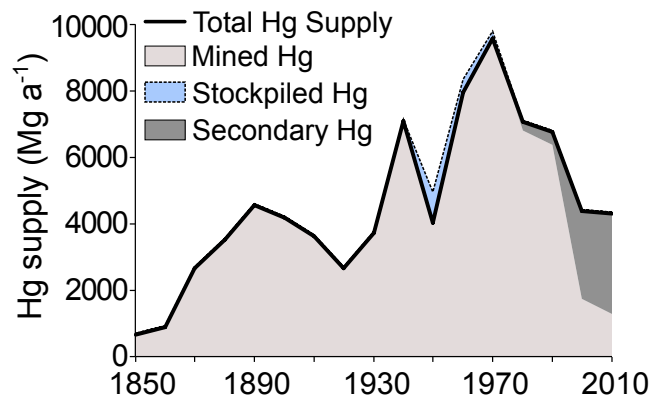
526
527 **Figure 1. Historical global supply of Hg for commercial uses.** This supply includes primary
528 mined Hg (1850 – 2008 data from Streets et al.[10]), minus the amount stockpiled by the United
529 States between 1945 and 1970, and augmented by secondary Hg including recycled, recovered as
530 a byproduct, and released from stockpiles after 1980.

531

Table 1. Intentional uses of Hg in products and processes.

| Category name	Description
Chlor-Alkali Plants	Electrochemical production of caustic soda and chlorine with Hg cathode
Silver and Large-scale Gold Mining	Extraction from ore by Hg amalgamation
Artisanal and Small-Scale Gold Mining (ASGM)	Hg amalgamation by individual miners
Vinyl Chloride Monomer (VCM) and Other Chemical	Production of chemicals with Hg catalysts, felt hat manufacturing, and laboratory uses
Paint	Hg fungicide in marine anti-fouling paint, interior and exterior latex paint
Lamps	All types of Hg-containing lightbulbs (fluorescent, high intensity discharge, etc.)
Batteries	Button cells and cylinders using Hg as cathode or to prevent corrosion
Wiring Devices and Industrial Measuring Devices	Switches and relays, thermostats, barometers, manometers
Medical Devices	Thermometers and sphygmomanometers (blood pressure meters)
Pharmaceuticals and Personal Care Products	Vaccines and medicines, soaps, cosmetics
Dental amalgam	Cavity fillings with Hg/silver/tin/copper amalgam
Dyes/Vermilion	Pigments containing Hg compounds
Pesticides and Fertilizer	Fungicides used in agriculture and pulp and paper
Explosives/Weapons	Munitions, blasting caps, fireworks
Other	Ritual, cultural, and miscellaneous uses

533
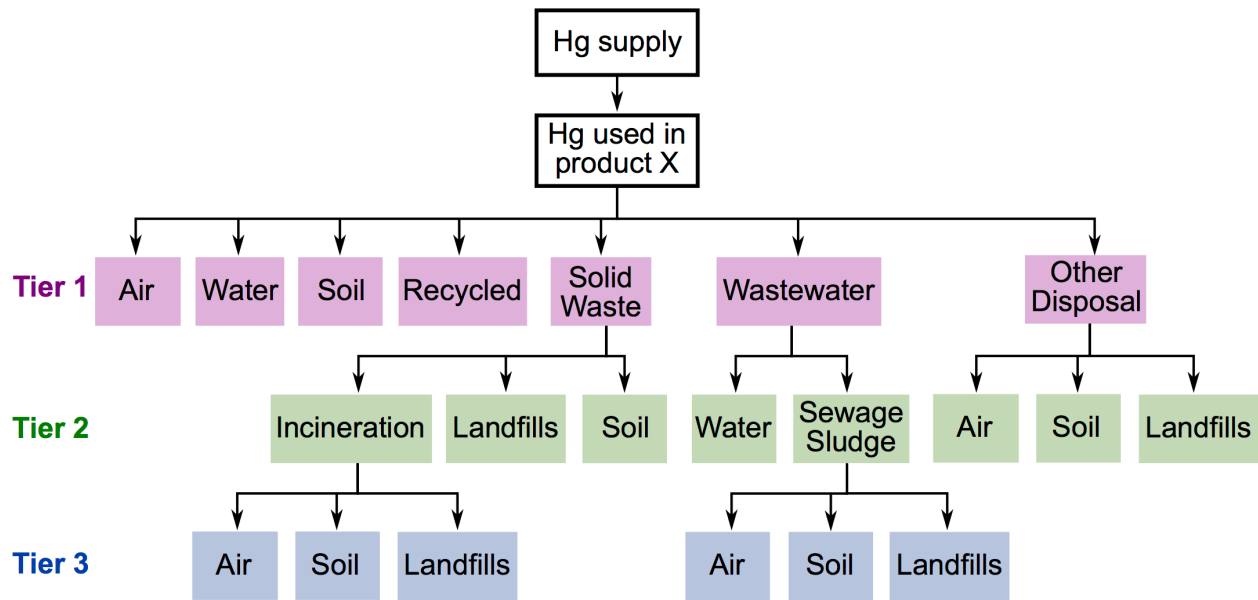
534
535
536 **Figure 2. Generic substance flow analysis diagram for commercial Hg.** Each arrow is a
537 distribution factor quantified in this work (Table S3). This diagram applies to all intentional use
538 categories with the exception of dental amalgam, which has additional pathways (see Methods).
539 "Other disposal" refers to medical waste incineration (for Medical Devices and Dental use
540 categories) and iron and steel recycling (for Wiring Devices and Industrial Measuring Devices
541 use category).
542
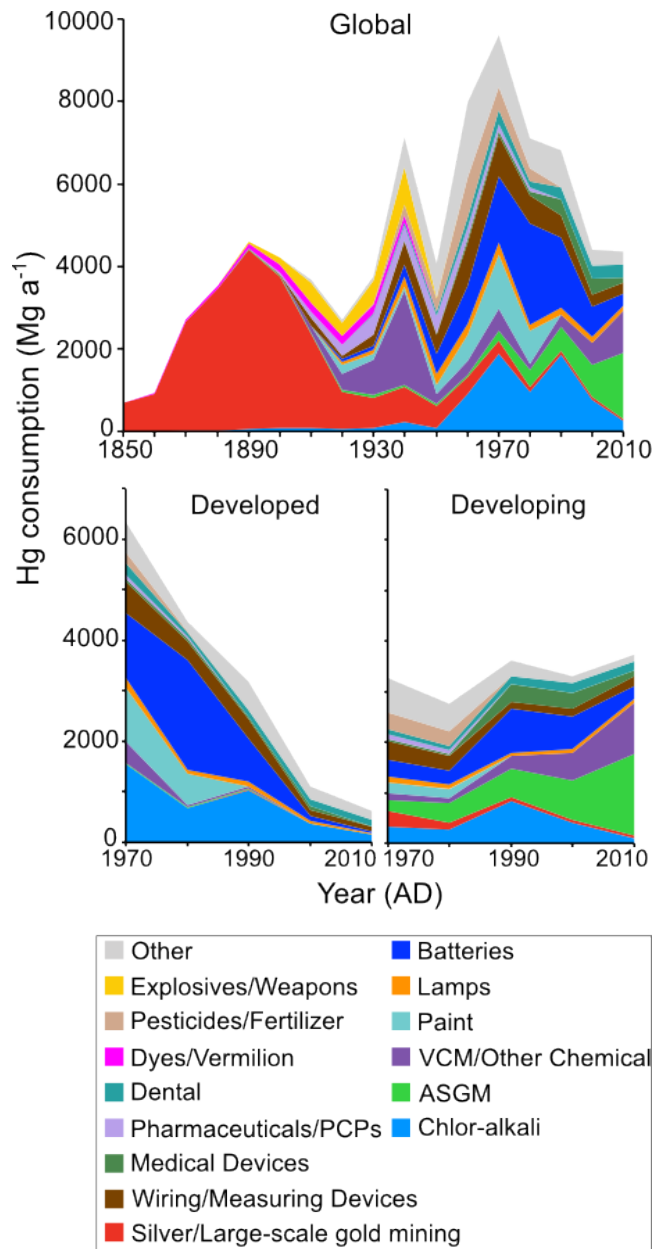
543
Figure 3. Global historical Hg consumption in commercial products. Consumption is
partitioned for each decade between the different use categories of Table 1, and further
partitioned between developed countries and developing countries after 1970.
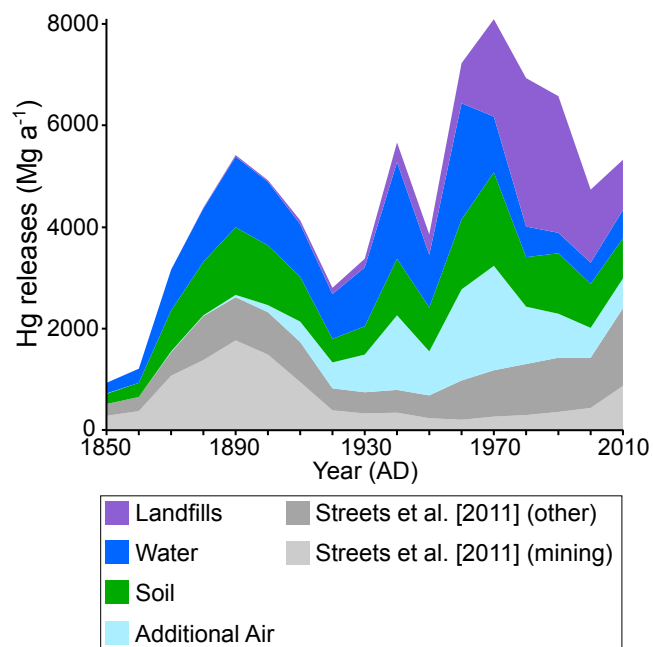
Figure 4. Historical global releases of Hg to the environment. The Streets et al.[10] inventory includes atmospheric releases from combustion, smelting, mining, and chlor-alkali plants. Additional air, soil, water, and landfill releases shown are associated with commercial Hg products as quantified in this work.
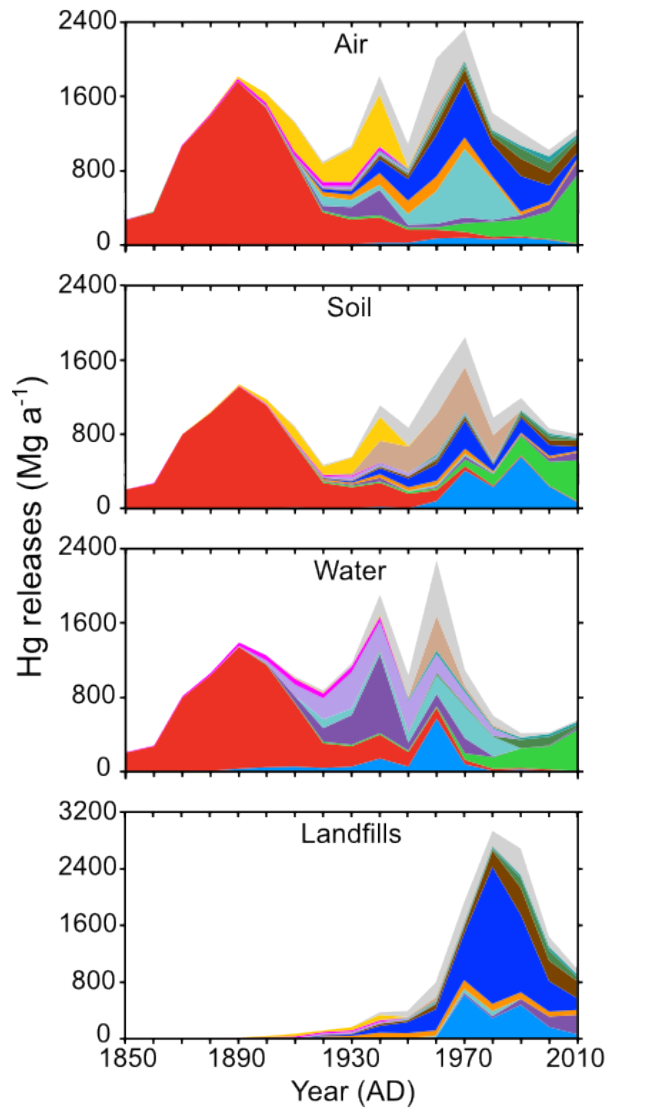
552
553 **Figure 5. Global historical releases of commercial Hg to environmental reservoirs by use**
554 **category.**
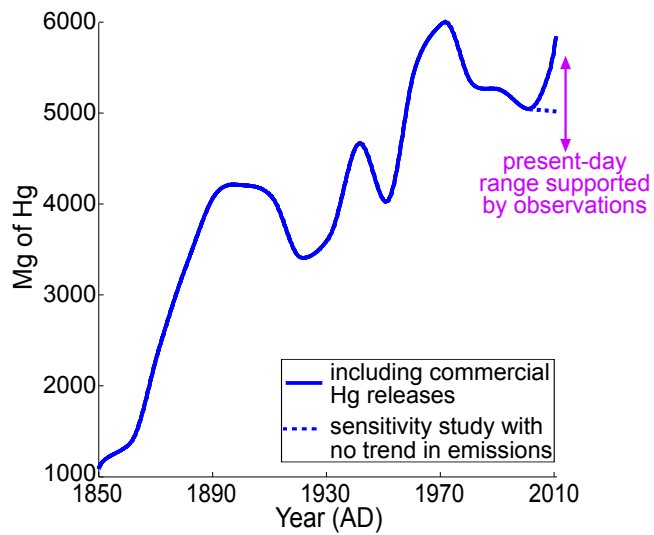
555
556 **Figure 6. Trend in simulated atmospheric Hg mass from 1850 to 2010.** Results shown using
557 the updated biogeochemical model described in the text, including additional commercial Hg
558 releases (blue) and a sensitivity simulation with ASGM releases and Streets et al.[10]
559 anthropogenic atmospheric emissions held constant from 2000-2010 (dotted blue line).