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Uncertainties in Atmospheric Mercury Modeling for Policy Evaluation

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Abstract Mercury (Hg) contamination is an issue of a growing environmental and public health concern. Atmospheric chemistry transport models for Hg are a critical tool for understanding the sources, processes, and fate of Hg. Uncertainties in multiple aspects of atmospheric Hg models, however, limit their application for policy evaluation and for monitoring global trends in atmospheric Hg concentrations. This review aims to identify uncertainties in atmospheric Hg modeling that are relevant in the context of policy and for informing decision-making. We focus on specific requirements of the Minamata Convention on Mercury, a global treaty signed in 2013 to protect human health and the environment from Hg, to demonstrate how existing uncertainties in atmospheric Hg modeling can influence our ability to evaluate source-receptor relationships. Modeling studies of source attribution suggest that major uncertainties in atmospheric Hg modeling arise from anthropogenic emissions, biogeochemical cycling, and atmospheric chemistry. Uncertainties in these aspects of modeling are expected to increase under the Convention, with regulation of anthropogenic emissions, changes in atmospheric conditions, and legacy and natural Hg source contribution to the global biogeochemical cycle. These uncertainties can interact with one another and with the current Hg species measurement capability and pose challenges to effectively monitoring trends in atmospheric Hg. Developing additional means to attribute simulated atmospheric Hg trends and improve source-receptor relationships in atmospheric Hg models would improve our ability to evaluate the Convention's effectiveness.

Introduction

Mercury (Hg) is a widely distributed toxic trace element that can be released to the environment from natural and anthropogenic sources [1]. In the atmosphere, Hg most commonly exists in the form of gaseous elemental Hg (Hg^0), which has an atmospheric lifetime of ~0.5–1 year [2]. Oxidized Hg species (Hg^{2+}, Hg^P) are highly reactive and water-soluble, and can deposit to ecosystems through precipitation (wet deposition) or as dry deposition. Once Hg is deposited, the toxic and bioaccumlative monomethylmercury (MMHg) can be formed and pose significant health risks to humans and wildlife upon bioaccumulation [3, 4]. Understanding the transport, chemistry, and deposition of atmospheric Hg is critical to effectively managing these risks.

Atmospheric chemistry transport models for Hg are a critical tool for understanding the sources, processes, and fate of Hg. Atmospheric models have been used extensively for assessing speciation, transport, and deposition of various atmospheric Hg species at both regional [5–17] and global scales [18–25]. Atmospheric models are increasingly being

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used to interpret global trends in atmospheric Hg concentrations [26, 27] and to project future changes in Hg emissions and deposition under various policy and technology scenarios [28, 29••, 30]. Despite the increasing use of models for these applications, uncertainty in our ability to model the global biogeochemical cycling of Hg poses challenges to interpreting modeled results. For instance, Corbitt et al. [28] found that the uncertainties in emissions, chemistry, and fate of Hg upon deposition to surface reservoirs pose significant challenges to linking Hg sources to receptors on a global scale. Inter-model [16, 31–34] and model-observation comparison studies [7, 11, 19, 21, 35, 36] have also collectively demonstrated that the existing uncertainties in multiple components of atmospheric Hg models can lead to considerable discrepancies between Hg simulations and in comparisons with observed atmospheric Hg concentrations and deposition.

The Minamata Convention on Mercury, a global treaty signed in 2013 to protect human health and the environment from Hg, will lead to multiple policies and technologies that can lead to upstream removal of Hg [37••]. For example, one study projected that Minamata Convention-specific technology modification scenarios in Indian and Chinese coal-fired power plants could substantially change the extent of Hg emission and the impacts of deposition worldwide, depending on the types of pollution control strategies employed [29••]. Under these changing conditions, evaluating the effectiveness of policies and technologies will depend on the ability to establish a precise source-receptor baseline in the absence of changes, and to quantify changes on multiple spatial and temporal dimensions. Specific provisions have been included to evaluate the effectiveness of the Convention (*Article 22*)

and to monitor Hg cycling, and fate in a range of ecosystems taking account of the differences among Hg sources (*Article 19*).

The objective of this paper is to review the uncertainties in atmospheric Hg modeling that are relevant in the context of policy, specifically focusing on the Minamata Convention on Mercury. A number of previous studies and reviews have investigated uncertainties in atmospheric Hg modeling in diverse aspects of atmospheric Hg science, ranging from atmospheric Hg chemistry to monitoring various forms of Hg species [11, 38••, 39–41]. Here, we build upon this previous work by examining how uncertainties in atmospheric Hg modeling affect its application for policy evaluation, in particular for linking sources to receptors. Linking Hg sources to receptors is important for identifying sources that are subjected to change and for distinguishing sources that are relevant to environmental and human health impacts. We focus on the use of modeling to inform decision-making, focusing on requirements in the Minamata Convention to identify and demonstrate how existing uncertainties in atmospheric Hg modeling can influence our ability to evaluate policies and mitigate Hg risks. In Section 2, we summarize the challenges of source attribution in the context of the Convention. Section 3 addresses three major sources of uncertainty in models—anthropogenic emissions, biogeochemical cycling, and atmospheric chemistry—with respect to the challenges they pose for policy evaluation (Fig. 1). Section 4 illustrates how these uncertainties interact when applied to interpreting atmospheric Hg trends. We conclude by identifying ways in which future studies can help improve our ability to inform policies.

Fig. 1 Uncertainties in atmospheric Hg modeling
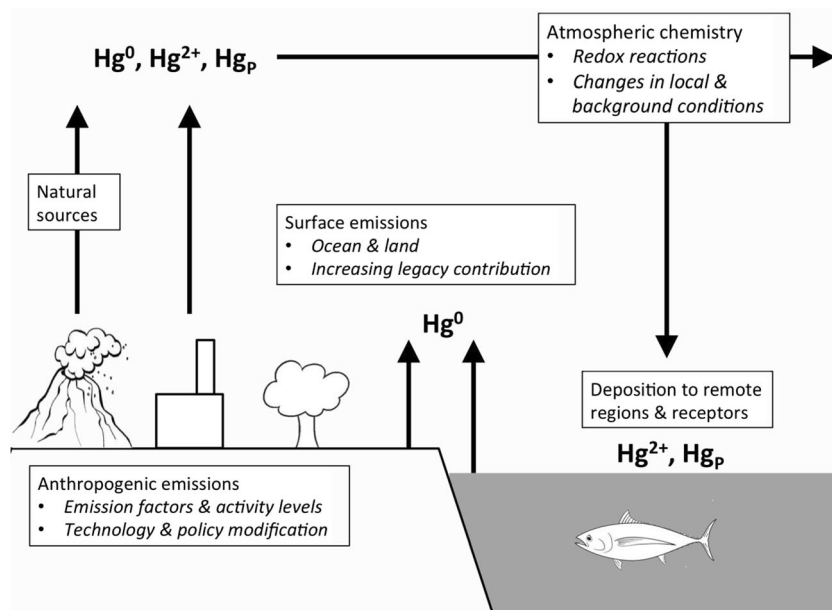
Source Attribution in the Context of the Minamata Convention

The Minamata Convention on Mercury includes provisions related to the production, use, trade, emissions, and releases of Hg [42•]. To monitor the effectiveness of the Convention, a periodic evaluation will be conducted on the presence and movement of Hg, as well as observed trends (*Article 22*). In order to understand whether the Convention has succeeded in protecting human health and the environment from Hg, actions on production, use, trade, emissions, and releases must be linked with resulting changes in concentrations in biotic media and populations. Linking emissions to impacts for Hg requires tracing a complex pathway from policies, through emissions, to eventual impacts [43]. Atmospheric modeling provides a first step in making this linkage, by tracing the link from emissions to deposition. Development and improvement in modeling are also specifically mentioned in the Minamata Convention as part of its provisions on cooperation in research, development, and monitoring (*Article 19*).

Source-attribution studies have been particularly useful for assessing the contribution and the potential changes of Hg emissions from various source regions to deposition in a receptor region [9, 28, 34, 44]. Previous work [34] evaluated the response of Hg deposition from source regions for the present and for future emission scenarios (i.e., Status Quo, Extended Emissions Control, Maximum Feasible Technological Reduction scenarios). Comparing multiple model estimates, they found that the largest sources of variability among modeled results were the uncertainties in chemical mechanisms governing the atmospheric speciation and in natural and secondary emissions originating from surface reservoirs. In another source-attribution study, Corbitt et al. [28] found that the simulated Hg deposition from a given source region for the present-day and future emission scenarios is sensitive to local and background components consisting of emission estimates, redox transformations, and fate of Hg

upon deposition to surface reservoirs. A recent intercomparison between three Hg models (GEOS-Chem, GLEMOS, and GMHG) [UNEP 2015] showed substantial differences in attribution of sources in some regions (Table 1).

Differences in attribution among various models can lead to very different policy conclusions. For example, in Europe, different models attributed fractional contributions of domestic deposition between 10 and 32 % (Table 1), with gross domestic deposition varying by more than a factor of three. These models further disagree on whether anthropogenic sources originating from within (domestic) or outside Europe (international) contribute a larger fraction of deposition to the European environment. In some areas, however, such as the Arctic, models are more consistent with each other, which is likely due to the lack of significant anthropogenic Hg emission sources located in these regions.

Uncertainties in Atmospheric Hg Models

The variability in estimates of source attribution among different analyses is driven both by differences in model assumptions and parameters and uncertainty in the underlying mechanisms that affect Hg behavior in the atmosphere. Atmospheric Hg models are built upon numerical models used to simulate climate, metrology, and air quality. By coupling emission estimates and species of various Hg sources and process level understanding of Hg cycling, over a dozen atmospheric Hg models have been developed in the past decade, which vary widely in the treatment of physical and chemical mechanisms, kinetics, reactants concentrations, and spatial domain [38••]. Below, we focus on three major areas of uncertainty that affect source-receptor analyses: anthropogenic emissions, biogeochemical cycling, and atmospheric chemistry.

Table 1 Domestic and international anthropogenic contributions to Hg deposition in selected global regions simulated by different global-scale Hg models

Region	GEOS-Chem		GLEMOS		GMHG	
	Domestic	International	Domestic	International	Domestic	International
Europe	20 %	18 %	32 %	20 %	10 %	23 %
North America	7 %	22 %	12 %	27 %	4 %	26 %
East Asia	35 %	11 %	55 %	11 %	23 %	13 %
South Asia	24 %	16 %	36 %	18 %	14 %	21 %
Southeast Asia	9 %	22 %	15 %	24 %	4 %	24 %
South America	7 %	17 %	8 %	23 %	5 %	22 %
Africa	11 %	16 %	13 %	21 %	10 %	20 %
Arctic	1 %	25 %	1 %	33 %	1 %	29 %

From UNEP/AMAP 2015 [33]

Anthropogenic Emission Inventories

The Minamata Convention includes specific provisions to improve existing inventories of Hg use, consumption, and anthropogenic emissions (*Article 19.1.a*). The ability to link anthropogenic sources to receptors using atmospheric Hg models is dependent on accurate estimates of Hg entering the environment, species profile, and the spatial distribution of emissions. A recent inter-model comparison study showed that the differences in anthropogenic emissions estimates utilized by models have a significant impact on simulated atmospheric Hg deposition [34].

Anthropogenic Hg sources are characterized in atmospheric Hg models by emission estimates and Hg species profiles. Table 2 summarizes quantitative emission ranges reported previously for different anthropogenic sectors and regions [45, 46]. The uncertainties reported here reflect cumulative uncertainties in emission factors and activity levels, which are used to derive emission estimates for each anthropogenic sector and region.

Anthropogenic Hg emission inventories report a large range of values for various sectors (Table 2). Ranges reported for stationary fossil fuel are relatively lower, related to the accuracy of emission factors in various fuels and control measures applied to power plants. The magnitude of artisanal and small-scale gold amalgamation activities, in contrast, is very poorly understood [30]. On a regional basis, quantitative ranges for anthropogenic emissions have been reported worldwide (Table 2). For many countries, however, emission factors and activity levels are derived from extrapolation of existing information, since no measurements or statistical information are

Table 2 Summary of quantitative emission ranges reported for different anthropogenic sectors and regions

	Range (%)
Sector	
Stationary fossil fuel combustion	−36/+65
Non-ferrous metal production	−58/+242
Iron and steel production	−55/+81
Cement production	−62/+273
Waste disposal and incineration	−75/+245
Mercury production	−41/+52
Gold production	−99/+153
Region	
Africa	−47/+67
Asia	−49/+118
Australia	−78/+136
Europe	−63/+158
North America	−43/+129
South America	−48/+90

From UNEP [33]

available to make accurate point source emission estimates. The assumptions made for assigning countries to particularly regional-grouping, specific technology, and waste-handling procedures can also introduce uncertainties in emission estimates. A recent study reported that, in China alone, the overall uncertainty in the emission inventory ranges from −20 % to +23 % depending on the availability of domestic information [47]. The relatively large regional uncertainties reported in Africa and South America are most likely due to the widespread artisanal and small-scale gold amalgamation activities, indicating that the uncertainties associated with different anthropogenic sectors can also contribute to the regional uncertainties.

Quantitative assessments of uncertainties in Hg emissions speciation have been limited, but recent studies suggest that the Hg speciation prescribed in atmospheric Hg models may be inaccurate. Measurements of Hg species originating from coal combustion sectors have shown wide ranges in Hg species ratio depending on the emission control devices, Hg content in coal, and coal characteristics [48–52]. Zhang et al. [36], in a model-observation comparison study using the GEOS-Chem model, observed significant over prediction in wet deposition from regions of high anthropogenic emissions. Similarly, using the GRAHM model, Kos et al. [11] found that by altering the prescribed $Hg^0/Hg^{2+}/Hg_P$ ratio to 90:8:2, the model was able to reproduce observed surface air concentrations in the USA. Models included in the 2015 UNEP/AMAP intercomparison [33] used speciation breakdowns ranging from 81 to 96 % for Hg^0. For sectors such as nonferrous metal smelting, Hg species profile showed considerable differences depending on the metal produced (zinc, lead, copper) [53]. A recent measurement of Hg species liberated during municipal solid waste incineration also showed a $Hg^0/Hg^{2+}/Hg_P$ ratio of 95.5:4.1:0.4 [54], which is substantially different from the Hg species profile assigned to waste incineration in landfills in inventories of 20:60:20 [45].

Uncertainties in different anthropogenic sectors and regions have an additive influence on the overall anthropogenic emission estimates and can introduce methodological variability for deriving anthropogenic emission inventories. Muntean et al. [30] provided a comprehensive comparison between two anthropogenic emission inventories: EDGARv4 and AMAP/UNEP (2008). The major differences were documented from key anthropogenic sectors, which were represented by different aggregated subsectors and regional compositions, and the methodologies employed for deriving activity levels and emission factors. The AMAP/UNEP estimate of the global anthropogenic Hg emission (1785 t) is over 50 % higher than the EDGARv4 estimate (1172 t). Muntean et al. [30] showed that the largest difference was in the residential sector, due to higher AMAP/UNEP emission factors assigned to technologies and coal types used in combustion sectors. In addition, sources not fully captured by these inventories may have

a substantial influence on the global biogeochemical cycle. Horowitz et al. [55], for example, argued that Hg in commercial products and its release to various geochemical reservoirs can be substantial historical and present-day sources of Hg emissions.

Under the Minamata Convention, parties must apply Best Available Techniques and Best Environmental Practices to mitigate anthropogenic Hg emissions (excluding direct Hg mining activities and chlor-alkali industries) (*Article 8*). While the Convention's flexibility takes into account domestic technical capacity and economic development plans, we expect the existing uncertainties in anthropogenic emission inventories to increase with large-scale and regionally variable abatement efforts under the Convention. Continuous improvement in anthropogenic emission inventories reflecting technology and policy changes over time will become essential for quantifying changes on multiple spatial and temporal dimensions.

Biogeochemical Cycle

An additional uncertainty affecting source-receptor analyses in models is how natural (i.e., primary geogenic, emissions from land and ocean) and legacy Hg sources (i.e., recycling of previously deposited anthropogenic Hg) are treated. A major uncertainty involves what fraction of present-day deposition is contributed by current anthropogenic sources (which are subject to regulatory requirements) relative to the legacy and natural fraction. Distinguishing the relative importance of these source contributions is important in two ways. First, the anthropogenic fraction provides a constraint on how Hg deposition is affected by source reductions. Second, the legacy fraction, in the context of past anthropogenic emissions, contains information on the timescales of how the global biogeochemical cycle responds to changing emissions. Accurate representation of these sources contributions in Hg models is also expected to be important for the Convention's provision on the monitoring of Hg cycling, transformation, and fate of various Hg sources (i.e., anthropogenic, natural, legacy; *Article 19.1.e*).

Quantifying the legacy contribution to the global biogeochemical cycle requires constructing both natural and present-day Hg biogeochemical cycles. Earlier modeling efforts used lake sediment archives to constrain preindustrial deposition relative to present day, and found that deposition had been enhanced by a factor of 3–5 since preindustrial times [25, 56, 57]. Amos et al. [58] suggested that anthropogenic activities prior to the Industrial Revolution contributed substantially to legacy Hg and estimated that deposition is enhanced by a factor of 7.5 relative to natural levels. There is ongoing controversy in the literature about the importance of preindustrial anthropogenic emissions—particularly from mining—and their importance for the present-day biogeochemical cycle of Hg [59–62].

Overall, however, models agree that globally, the combined contribution of natural and legacy Hg to deposition is larger than the contribution from direct anthropogenic sources [21, 25, 58]. A recent study that identified challenges for implementing the Convention suggested that the reduction in anthropogenic Hg emissions would have a small initial influence on the global atmospheric and oceanic Hg pools due to the recycling and deposition of legacy Hg [37••]. Applying future emission scenarios consistent with Minamata Convention requirements, the study projected consistent Hg concentrations in the atmosphere and surface ocean in the low-emission scenarios and significant increases (75 % in the atmosphere, 50 % in surface ocean) in the high-emission scenarios relative to the present. With future policies to control Hg, the contribution of natural and legacy Hg may increase in the global atmospheric Hg pool relative to anthropogenic sources. Unfortunately, the natural and legacy Hg emissions inputs to models currently demonstrate factor of five differences [34]. Sensitivity simulations conducted by Amos et al. [63] of historical atmospheric emissions and model rate coefficients on present-day reservoirs have shown that the largest uncertainties in quantifying the legacy contribution arise from parameterizations of air-sea exchange, retention of Hg in soil, and disturbance of coastal sediments.

Multiple types of biogeochemical cycle models for Hg have been developed over the past several decades to estimate various Hg source contributions to the global Hg budget. Coupling of these models to atmospheric chemistry transport models has provided a basis for simulating Hg emissions from surface reservoirs. Early models included dominant geochemical reservoirs by extrapolating from sparse flux measurements or by imposing mass balance constraints [57, 64, 65]. Other models have used first-order rate constants or physical laws of equations to build mechanically based representations of surface and exchange fluxes between reservoirs [12, 20, 25, 56, 63, 66]. Some recent models have a more explicit representation of Hg biogeochemistry, adjusted by empirical bulk transformation rates between Hg species or compensation points [67–70, 71•]. A few efforts have linked global atmospheric models with land and ocean simulations to address the effect of legacy Hg at decadal to century-long time scales [71•, 72]. Smith-Downey et al. [72] used a carbon biogeochemical cycling model to parameterize Hg partitioning and turnover dynamics to resolve the magnitude and the time-scale of Hg recycling from deep soil. Zhang et al. [71•] linked the atmospheric model GEOS-Chem to a global ocean model of Hg to simulate long-term accumulation of anthropogenic Hg.

Uncertainties in estimating present-day natural and legacy emissions from land and ocean arise from lack of mechanistic understanding and kinetics governing emission processes, and limited measurements available for model validation. Representations of mechanistic processes governing Hg flux from terrestrial ecosystems exhibit considerable variation

across models. Improvement of existing models will require knowledge of the processes governing the net emission under various environmental conditions, contamination levels, and ecosystem types. Net emissions are driven by spatiotemporally variable processes that govern both flux to the atmosphere, and deposition processes such as litterfall, throughfall, and direct atmospheric Hg deposition [73]. A compilation of Hg flux measurements has shown that the interaction of multiple factors such as land cover, land cover type, and Hg contamination can determine the extent of Hg emissions from land, where the net Hg fluxes result in decreasing order from mining areas, naturally enriched Hg belt, atmospherically influenced soil, contaminated soil, and background soil [74]. Moreover, the study found that areas impacted by large atmospheric deposition often display ten times higher Hg flux compared to background sites. In terrestrial ecosystems, Hg emissions have been parameterized in models as a function of solar radiation, temperature, and soil moisture. Lin et al. [75] used inventories for other gases (i.e., VOC, NOx) to derive Hg emissions from different land cover types. Other models have used simple kinetics and physical laws of equations to estimate Hg emissions from different terrestrial components (i.e., bare soil, soil under canopy, water) [76]. Bash et al. [67] developed a dynamic bidirectional exchange model by employing the compensation point and resistance concepts to air-canopy, air-water, and air-soil exchange. Global estimates were provided by Selin et al. [25], who compartmentalized emission processes to prompt recycling, slow soil volatilization, and evapotranspiration. Similar methods have been adopted by other studies to estimate Hg emissions from terrestrial ecosystems (ECHMERIT, CAM-Hg) [12, 20]. A recent top-down estimate of fluxes based on Hg^0 measurement data constraints estimated uncertainty range of ±51 % for soil emissions and ±63 % for ocean [77].

Primary geogenic sources include emission from geologically enriched areas as well as volcanoes. Hg emissions from volcanoes are often derived from Hg/SO_2 ratios and SO_2 emission inventories due to the difficulty of obtaining Hg measurements from these sources. A compilation of Hg/SO_2 ratios from volcanic gases has shown an order of two magnitude difference depending on the volcano types [78]. Similar ratio-based methods and inventory of CO emissions are used to estimate Hg emissions from biomass burning. The Hg/CO ratios have shown significant variability across vegetation types and an order of magnitude difference for a given biome [79]. By applying three different Hg/CO ratios (average, biome- and land cover-specific), a recent study found a wide range of 302 to 599 Mg/year in the global estimates of Hg emissions from biomass burning [80]. Applying different CO emission inventories, De Simone et al. [80] found that simulated resulting Hg deposition fluxes have significant hemispheric and annual differences.

Hg exchange between the atmosphere and ocean is affected by wind speed, solar radiation, temperature, and primary productivity. By applying these variables, previous studies have used CO emission inventories [81] or assigned constant dissolved gaseous Hg concentrations to estimate Hg emissions [10]. Simplified two-dimensional slab ocean models [26, 68] have been linked with global atmospheric Hg models (GEOS-Chem) to resolve air-sea exchange, mixed layer biotic and abiotic redox transformations, and vertical transport via particle settling but do not resolve horizontal transport. While the contribution of riverine Hg to the global atmosphere is relatively small in comparison to oceans, a recent study that implemented riverine and terrigenous Hg input to GEOS-Chem has shown that the contribution of these sources and subsequent reemission from ocean surfaces may be important both regionally and seasonally (i.e., summer maxima of Hg^0 in the Arctic) [82]. Similar kinetic approaches have been implemented by other studies (ECHMERIT, CAM-Hg) [12, 20] which produced comparable results with the measured surface ocean Hg^0 [83]. Surface water redox kinetics and partition coefficients used to calculate surface emissions and removal to deep ocean are typically derived from in situ experiments from coastal water due to the difficulty of obtaining empirical measurements from the open ocean. Sensitivity simulations have demonstrated that model rate coefficients and Hg measurement inputs have significant impact on the modeled Hg fluxes. Qureshi et al. [84], based on a global multimedia model, suggested that uncertainties in redox reactions in the surface ocean contribute more than uncertainties in anthropogenic emissions to total uncertainties in atmospheric concentration and deposition fluxes of Hg. Using the ranges of experimentally derived partition coefficients between Hg^{2+} and particulate matter, Zhang et al. [71•] found that 50 % variation in the partition coefficient can result in 10–20 % variation in the amount of Hg sinking to the deep ocean. Sunderland and Mason [85] showed that the variability in the observed fraction of dissolved Hg^0 in the surface water column accounts for 48–66 % variance in modeled seawater concentrations. Complex parameterizations of ocean biogeochemistry will require extensive measurement and experimental data to evaluate modeled outputs across time and space.

Atmospheric Chemistry

The Minamata Convention includes provisions to improve information on long-range transport, transformation, and deposition of atmospheric Hg (*Article 19.1.e*). Changes in both local and background atmospheric conditions are expected to occur under the Convention (i.e., regulation of upstream emissions, large-scale reduction in anthropogenic emissions, and associated Hg reactants), which may influence our ability to link sources to receptors on a global scale. Accurate representation of the chemical transformations that Hg undergoes in

the atmosphere is thus important to linking Hg sources to receptors under various atmospheric conditions. The chemical mechanisms and the kinetics assigned to both regional and global atmospheric Hg models currently demonstrate significant variability [38••]. The concentrations of some Hg reactants such as Br, which are most often simulated from atmospheric chemistry models, are also not well constrained by measurements. Sensitivity analyses and inter-model comparison studies are increasingly being performed as a part of atmospheric Hg modeling studies to reveal uncertainties and constrain important chemical mechanisms governing Hg speciation, transport, and deposition [11, 21, 23, 31, 32, 34–36, 86]. The results from these studies collectively suggest that the uncertainties in the kinetics of Hg^0 oxidation and mechanistic uncertainties in Hg^{2+} reduction pose the greatest impact on simulated atmospheric Hg concentration and deposition.

Oxidation is the dominant mechanism responsible for the atmospheric removal of Hg^0. The dominant pathway for oxidation of Hg on the global scale is thought to be in the gas phase. Before 2010, modeling studies generally assumed that O_3 and OH were the primary oxidants for atmospheric Hg^0. A growing consensus from both model and experimental results suggests that Br is the dominant oxidant of Hg [87]. However, several models still use O_3 and OH chemistry to simulate Hg [12, 33]. Implementation in global scale Hg models of oxidation mechanisms using O_3 and OH can reproduce the patterns of observed global Hg behavior [23–25]. A compilation of experimental studies has shown wide ranges in reaction coefficients for both O_3 (3×10^{-20} to 2×10^{-18} cm^3 molecules^{-1} s^{-1}) and OH (5×10^{-16} to 1×10^{-13} cm^3 molecules^{-1} s^{-1}). These ranges have been attributed to the differences in experimental techniques (i.e., relative, absolute) and potential laboratory and environmental interferences (i.e., humidity, pressure, presence of sunlight, interaction with other compounds, and reactor walls) [41, 87]. However, theoretical calculations have suggested that these reactions are unlikely to be important oxidative pathways for atmospheric Hg^0 [87].

Mercury oxidation via Br is a well-established phenomenon during Atmospheric Mercury Depletion Events (AMDEs) in polar regions [88]. Experimental [89, 90] and theoretical calculations [91, 92] suggest that Hg^0 undergoes a thermodynamically favorable oxidative pathway in the presence of Br, where HgBr generated from the first reaction can either dissociate or react with other species including Br, OH, BrO, HO_2, and NO_2 to form stable oxidized Hg species. Recent modeling studies have shown that Br oxidation can explain the major features of global Hg behavior [21, 93]. Measurement and modeling studies have also associated elevated Br levels with enhanced Hg oxidation in the free troposphere [94, 95].

Atmospheric reduction of Hg^{2+} to Hg^0 is an important mechanism governing the residence time and the long-range transport of Hg^0 in the atmosphere. Laboratory experiments have shown that photoreduction of Hg^{2+} can occur in the aqueous phase by dissolved organic acids [96, 97]. This reduction mechanism was incorporated in the Community Multiscale Air Quality (CMAQ) Hg model by Bash et al. [6], who showed that this process improved model representation of wet deposition in the USA. Some models use a mechanism that involves reduction via HO_2; however, this mechanism is thought to be unlikely under most atmospheric conditions [98]. In other atmospheric models, the rate of reduction is adjusted to maintain consistency between modeled and measured atmospheric concentrations. Holmes et al. [21] documented a significant improvement in modeled results by increasing empirical photochemical reduction rates in the cloud water by a factor of 4. Seigneur et al. [23] found that atmospheric Hg models were unable to reproduce observed Hg^0 concentrations without the aqueous-phase Hg^{2+} reduction via HO_2. In another study, Shah et al. [99] found that in-cloud reduction was necessary to compensate for the fast oxidation via Br and to simulate measured distribution of Hg^{2+} in the atmosphere.

In addition to aqueous-phase reduction, rapid reduction has been proposed to take place directly in anthropogenic plumes [13, 17]. This mechanism was initially proposed by Lohman et al. [13], who suggested that a fraction of Hg^{2+} released from coal combustion is rapidly reduced to Hg^0 through gaseous-phase heterogeneous reduction via SO_2. This mechanism has been suggested as a possible explanation for the model-model and model-observation deviations observed near anthropogenic emission regions [11, 18, 36, 100]. Based on the wide ranges of Hg species ratios measured from coal combustion sectors [48–52], it is possible that in-plume reduction may also contribute to the uncertainties in Hg species profile assigned to anthropogenic emission inventories (*Section 3.1*). In the context of the Convention, changes in local atmospheric conditions can occur in regions with large anthropogenic emissions given the Convention's target to regulate upstream emissions. A previous study has shown that the magnitude of in-plume reduction is related to emission control devices as well as coal composition [48, 50, 101]. Given that emission inventories rely on in-stack measurements for emission rates and species input, any changes in in-plume reactions will affect the accuracy of the model dispersion and deposition estimates.

Uncertainties in Monitoring Hg Trends

The effectiveness evaluation provisions of the Minamata Convention (*Article 22*) coincide with the interest of applying atmospheric Hg models to evaluate recent changes in atmospheric Hg concentrations [102, 103]. A compilation of annual median total gaseous Hg concentrations from the Northern (Mace Head, Ireland) and Southern Hemispheric Hg monitoring stations (Cape Point, South Africa) has shown an average of 1.8 % per year and 1.25 % per year reduction, respectively,

in the past 2 decades [103]. In recent years, Southern Hemisphere Hg has begun to increase [104]. Wet deposition has shown consistent declining trends over North America [105]. Cumulative changes in atmospheric Hg concentrations suggest potentially significant changes in the Hg biogeochemical cycle. Multiple hypotheses have been proposed to explain the change in atmospheric Hg concentrations, which include changes in anthropogenic emissions, legacy Hg, and emissions from ocean and soil [26, 27, 103]. These sources overlap with the major sources of uncertainty discussed in the previous sections. Below, we demonstrate how the atmospheric modeling uncertainties discussed above interact when applied to interpreting atmospheric Hg trends.

Uncertainties in the magnitude and speciation of anthropogenic Hg emissions over time interact with atmospheric chemistry to affect the attribution of trends. Particularly relevant is the interaction of speciation and in-plume reduction. The anthropogenic Hg emission inventory developed by Muntean et al. [30] demonstrated that Hg^0 contribution to the total global Hg emissions have grown continuously between 1970 and 2008 due to artisanal and small-scale gold amalgamation activities. A contrasting result has been observed from another study, which used a different anthropogenic Hg emission inventory and observed a significant Hg^0 to Hg^{2+} shift in Hg species between 1850 and 2008 [106]. By applying the same anthropogenic emission inventory in an atmospheric model, Corbitt et al. [28] found that the fraction of Hg deposited from local anthropogenic sources in the form of Hg^{2+} will likely increase in the future. It is important to note, however, that in-plume reduction can affect the impact of emissions changes by altering the residence time of Hg in the atmosphere. In another study, Zhang et al. [27] modified emission inventories for Hg-added products, gold mining activities, and fossil fuel combustion sectors to reflect recent changes in anthropogenic activities and technology modification. By employing modified emission inventories in an atmospheric Hg model, the study found consistent declining trends in atmospheric Hg concentrations. Importantly, however, these modifications contrast with the currently available anthropogenic emission inventories, which estimate overall increases in anthropogenic emissions [30, 45].

Interpreting trends is also affected by the uncertainty surrounding timescales of Hg cycling in the atmosphere-land-ocean system, and their interaction with historical emissions estimates. For example, Soerensen et al. [26] used a small set of subsurface ocean Hg concentrations to simulate changes in atmospheric Hg over the North Atlantic Ocean and found an 80 % reduction in oceanic evasion in the past two decades. Based on this result, they suggested that the reduction in ocean Hg evasion may be responsible for the declining trend in atmospheric Hg concentrations. However, this requires that historical inputs to the ocean be larger than prior estimates. Constraints on ocean Hg content from measurements and

correlations with other trace elements suggest smaller historical inputs [107]. Uncertainties in simulating ocean Hg cycling also interact with atmospheric chemistry uncertainties. Song et al. [77] found that parameters in the GEOS-Chem model controlling ocean Hg behavior were strongly correlated with atmospheric chemical parameters, limiting the ability for measurement data to constrain either of these processes.

In addition to uncertainties discussed previously, another source of uncertainty in using models to interpret atmospheric Hg trends is the measurement data itself [108•]. Comparisons of model simulation with measurement values have served as a central test for evaluating model performance. Particularly in the context of monitoring Hg trends, extensive measurement data, in the form of long-term coordinated monitoring stations, can be useful for validating and refining the simulated atmospheric trends in Hg. However, existing monitoring networks have substantial limitations. Measuring different forms and species of Hg face analytical challenges and are subject to environmental interferences [39, 108•]. The predominant chemical form of Hg^{2+} in the atmosphere remains unknown and is measured via operationally determined methods. Quantifying Hg flux from the ocean is also sensitive to a small subset of measured seawater concentrations [85]. Comparability of measurements across different sites and networks limits the application of quantitative techniques to Hg models [77]. Lack of coordinated measurement networks that are representative of different global regions, multiple ecosystem types, environmental conditions, anthropogenic sources, and contamination level poses major gaps in our ability to assess the effects of large-scale changes in atmospheric Hg concentrations on the changes of ecosystem and human health impacts.

Taken together, the large-scale atmospheric trends of Hg of on the order of 1–2 % per year are small compared with the roughly 70 % uncertainty in surface-atmosphere flux, 30–50 % uncertainty in anthropogenic sources, and threefold model variability in attributable fraction (Table 1). On the whole, this suggests that scientific knowledge is not currently sufficient to attribute causes to changes of this magnitude [37••]. As efforts to curb anthropogenic Hg emissions increase, developing additional means to attribute simulated atmospheric Hg trends and improve source-receptor relationships would improve our ability to evaluate the Convention's effectiveness.

Conclusion

Hg contamination is an issue of growing environmental and public health concern. The Minamata Convention on Mercury, a global effort to protect the human health and the environment from toxic Hg, will introduce multiple policies and technologies that can lead to upstream removal of Hg on both domestic and international levels. Evaluating the effectiveness of such large-scale policy and technology changes

requires establishing a precise source-receptor baseline in the absence of changes and quantifying changes on multiple spatial and temporal dimensions. The uncertainties in multiple components of atmospheric Hg modeling however pose challenges to linking source-receptors and limit the applicability of atmospheric models for policy evaluation.

We reviewed the major sources of uncertainties in atmospheric Hg modeling in the context of the Minamata Convention. Major sources of uncertainties include the anthropogenic emissions inventory, biogeochemical cycles, and atmospheric chemistry. With increasing changes that are expected to occur under the Convention, the existing uncertainties in multiple components of atmospheric Hg models will likely exacerbate in the future. Regulation of anthropogenic emissions will influence our ability to accurately represent species and concentrations. We also expect the natural and legacy contribution to increase in the global atmospheric Hg pool; modeling of these source contributions is limited by mechanistic understanding and the kinetics governing the emission processes. Changes in atmospheric chemistry and climate may influence our ability to project the speciation, transport, and deposition of various Hg sources to receptor regions. With respect to interpreting and attributing changes in atmospheric Hg concentrations, improvement in the existing uncertainties of atmospheric Hg modeling and monitoring performances will become critical.

Several areas of research could contribute to improving source-receptor relationships in atmospheric Hg models. First, quantitative uncertainty analyses could better capture how uncertainty in models combines with measurements to influence projections. For example, quantitative techniques previously applied to Hg modeling to gain insight into processes include Monte Carlo uncertainty analysis [84] and Bayesian inverse methods [77]. Other techniques such as reduced-form modeling previously applied to analyses of other pollutants such as persistent organic pollutants [109] could also be applied to Hg modeling.

Another development that has potential to improve source-receptor relationships in models is advancement in the measurement of Hg stable isotopes. Hg stable isotope measurements have become a powerful tool for tracing Hg sources and understanding complex biogeochemical processes governing Hg in natural ecosystems. Hg isotopes can undergo mixing and fractionation by two types of pathways that impart distinct Hg isotopic compositions on natural environmental samples. Studies have shown distinct Hg isotopic compositions in samples those impacted by coal-fired power plants, metal refineries, and gold amalgamation [110–112]. Significant fractionations of Hg isotopes have been observed during AMDEs [88] and in-plume reduction [113] as well as in background atmospheric conditions via photochemical reduction, oxidation, and sorption to particles [114•]. Linking Hg

isotope measurements to box models has shown that the model can effectively reproduce Hg isotopic compositions in various surface reservoirs [115].

Improvements in measurement of Hg species should also be conducted in collaboration with model development. Better knowledge and reliable measurements of the speciation of Hg^{2+} in the atmosphere would dramatically improve our ability to quantify atmospheric chemical processes and emissions inventories. Concurrently, improvements in data on emissions, especially the speciation and capture efficiencies associated with control technologies, are necessary to more accurately project the impact of future policy. Increased attention to measurement comparability for Hg^0, as well as measurements in under-sampled locations, would improve our ability to use models to constrain emissions and processes.

Finally, it must be noted that atmospheric Hg uncertainties represent only one step in the conceptual pathway linking emissions to eventual impacts (Fig. 1). Uncertainties and variability in ecosystem responses, Hg intake, and health impacts can contribute substantially to overall uncertainty in assessing the benefits of policy [43]. Advances in atmospheric Hg modeling will need to be coupled to best-available Hg science from aquatic and terrestrial systems as well as social science to inform effective impact and policy assessment tools.

Compliance with Ethical Standards

Conflict of Interest   On behalf of all authors, the corresponding author states that there is no conflict of interest.

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•• Of major importance

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