

Review

Recent Advances in Atmospheric Chemistry of Mercury

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Abstract: Mercury is one of the most toxic metals and has global importance due to the biomagnification and bioaccumulation of organomercury via the aquatic food web. The physical and chemical transformations of various mercury species in the atmosphere strongly influence their composition, phase, transport characteristics and deposition rate back to the ground. Modeling efforts to assess global cycling of mercury require an accurate understanding of atmospheric mercury chemistry. Yet, there are several key uncertainties precluding accurate modeling of physical and chemical transformations. We focus this article on recent studies (since 2015) on improving our understanding of the atmospheric chemistry of mercury. We discuss recent advances in determining the dominant atmospheric oxidant of elemental mercury (Hg^0) and understanding the oxidation reactions of Hg^0 by halogen atoms and by nitrate radical (NO_3)—in the aqueous reduction of oxidized mercury compounds (Hg^{II}) as well as in the heterogeneous reactions of Hg on atmospheric-relevant surfaces. The need for future research to improve understanding of the fate and transformation of mercury in the atmosphere is also discussed.

Keywords: mercury; atmospheric chemistry; recent progress; future research needs

1. Introduction

Mercury (Hg) is one of the most toxic heavy metals commonly found in the global environment including the lithosphere, hydrosphere, atmosphere and biosphere. Due to the rather long lifetime of atmospheric mercury, once mercury compounds are released into the atmosphere, they can be transported around the globe. As such, they not only have local impacts but also regional and global implications [1,2].

Hg—atomic number 80—is a Group IIB transition metal with a closed shell electronic configuration ($5d^{10} 6s^2$). Elemental mercury (Hg^0) is the only metal in liquid form at room temperature and pressure. Due to the versatility of mercury, it is used as a catalyst, as an electrode material in electrochemistry, in optical spectroscopy, as a reflective liquid in liquid mirror telescopes and also in medicine, e.g., as amalgam in dental fillings. However, tragic outbreaks of mercury-induced diseases have occurred in many areas of the world particularly in Japan and Iraq over the years [3]. Mercury toxicity depends on its chemical species, with the methylated form being highly toxic. Exposure of humans and wildlife to mercury occurs primarily through fish consumption and to a much lesser extent through inhalation, drinking water and dermal contact. Exposure to mercury affects the human nervous system, hinders cognitive development in children and causes cardiovascular diseases in adults. In fish, mammals and birds, mercury can adversely affect reproductive behavior [4].

Atmospheric deposition had been identified as an important pathway for Hg transport into natural water and soil. It has been estimated that 5000–8000 metric tons of mercury are emitted per year into the atmosphere with three major sources from natural, anthropogenic and re-emitted sources [1]. Natural sources of Hg emission include volcanoes, soils, forests, lakes and open oceans and the largest anthropogenic source of Hg emission is coal burning in coal fueled power plants [5]. Through a series of physical, chemical and biological transformations in various compartments of the earth, previously deposited mercury could be re-emitted to the atmosphere [6,7]. Existing emission inventories are thought to be relatively accurate for anthropogenic emission source categories such as the energy and industrial sectors in the United States and Europe but with large uncertainties for other anthropogenic sources and even larger uncertainties for natural sources and re-emission estimation [8].

Figure 1a illustrates a simplified picture of mercury transformations in the environment, particularly on various environmental surfaces, and Figure 1b focuses on the atmospheric chemistry of mercury. In the atmospheric environment, mercury exists predominantly in the elemental form (oxidation state 0) and in the +2 oxidation state. Atmospheric Hg can be present in the gas phase, dissolved in cloud or fog droplets, or in the particulate phase (either as a component of primary particulate matter or adsorbed on existing particles). These various Hg species have different rates of dry and wet deposition and, subsequently, their respective atmospheric lifetimes differ significantly. For example, gaseous elemental mercury (Hg^0) has been estimated to have an atmospheric lifetime of about 1 year [3,9], which makes it subject to long-range transportation across the globe. Yet, atmospheric oxidation of Hg^0 to HgBr_2 will make mercury more subject to deposition, due to the low solubility of Hg^0 and high solubility of HgBr_2 in atmospheric droplets. The deposition of oxidized mercury could make Hg potentially become available to biota [3]. In the Arctic and Antarctic regions, after polar sunrise, field studies have demonstrated that gaseous elemental mercury is rapidly oxidized to Hg^{II} compounds, a phenomenon known as Arctic Mercury Depletion Events (AMDEs). The explanation of this interesting phenomenon will largely depend on fully understanding the oxidation/reduction pathways in the atmosphere [10]. On the other hand, numerical models of atmospheric transport and deposition are essential tools for interpreting field measurement data and evaluating abatement strategies and measures for pollution control. Further advancement of atmospheric Hg modeling relies on accurate kinetic studies on Hg chemistry, especially the oxidation and reduction pathways causing the transformation among various mercury species in the atmosphere. However, many of the key processes involved in the transformation and deposition of atmospheric mercury remain unidentified or un-quantified [11]. Global modeling studies suggest that there are large uncertainties in our understanding of the global mercury cycle [12].

The chemistry of atmospheric mercury was previously reviewed in detail by Lin and Pehkonen [13], Ariya, et al. [14], Subir, et al. [15], Lin, Singhasuk and Pehkonen [11] and Ariya, Amyot, Dastoor, Deeds, Feinberg, Kos, Poulain, Ryjkov, Semeniuk, Subir and Toyota [3]. Several excellent contributions have been made to our understanding in this area since 2015. The objective of this article is to discuss current understanding of atmospheric mercury chemistry, with more focus on recent laboratory, theoretical, field and model studies on the reactions interconverting Hg between elemental and divalent states. Finally, future research is recommended in order to better understand the dynamic transformations of atmospheric mercury.

Table 1. Current Accumulated Knowledge on Chemical Redox Pathways of Hg in the Gas Phase.

Gas phase Reaction.	Diluentgas ^a	Rate Coefficient ^b (cm ³ molec ⁻¹ s ⁻¹)	References
$Hg^0_{(g)} + Br_{(g)} \rightarrow HgBr_{(g)}$	Air, N ₂ , 1 atm	$(3.2 \pm 0.3) \times 10^{-12}$	[16]
	Air, NO, 1 atm	9×10^{-13}	[17]
	N/A, 1 atm	$1.01 \times 10^{-12} \exp(209.03/T)$	[2]
	N/A, 1 atm (298 K)	2.07×10^{-12}	
	N/A (180–400 K)	$1.1 \times 10^{-12} (T/298K)^{-2.37}$	[18]
	N/A, 1 atm (298 K)	1.1×10^{-12}	
	N ₂ , (243–298 K)	$(1.46 \pm 0.34) \times 10^{-32} \times (T/298)^{-(1.86 \pm 1.49)} \text{ cm}^6/\text{molec}^2/\text{s}$	[19]
	N ₂ , 1 atm (298 K)	$(3.6 \pm 0.9) \times 10^{-13}$	
	Ar, 1 atm	$9.80 \times 10^{-13} \exp[401(1/T-1/298)]$	[20]
	Ar, 1 atm (298 K)	9.80×10^{-13}	
Air, 1 atm	$(1.6 \pm 0.8) \times 10^{-13}$	[21]	
$HgBr_{(g)} + Br_{(g)} \rightarrow HgBr_{2(g)}$	CF ₃ Br, 0.26 atm	7×10^{-17}	[22]
	N/A, 1 atm (180–400 K)	$2.5 \times 10^{-10} (T/298K)^{-0.57}$	[18]
	N/A, 1 atm (298 K)	2.5×10^{-10}	
$Hg^0_{(g)} + Cl_{(g)} \rightarrow HgCl_{(g)}$	Ar, 0.93 atm	$(3.2 \pm 1.7) \times 10^{-11}$	[23]
	Air, NO, 1 atm	6.4×10^{-11}	[17]
	Air, N ₂ , 1 atm	$(1.0 \pm 0.2) \times 10^{-11}$	[16]
	N/A, 1 atm	$1.38 \times 10^{-12} \exp(208.02/T)$	[2]
	N/A, 1 atm (298 K)	2.81×10^{-12}	
	N ₂ (243–298 K)	$(2.2 \pm 0.5) \times 10^{-32} \times \exp[(680 \pm 400)(1/T-1/298)]$ cm ⁶ /molec ² /s	[24]
	N ₂ , 1 atm (298 K)	5.4×10^{-13}	
	N ₂ , 1 atm	1.2×10^{-10}	[25]
Air, 1 atm	$(1.8 \pm 0.5) \times 10^{-11}$	[21]	

$Hg^0_{(g)} + O_{3(g)} \rightarrow HgO_{(s)} + O_{2(g)}$	N/A, 1 atm	4.2×10^{-19}	
	N/A, 1 atm	4.9×10^{-18}	[26,27]
	Air, 1 atm	1.7×10^{-18}	[28]
	N ₂ /O ₂ , 1 atm	$(3 \pm 2) \times 10^{-20}$	[29]
	N ₂ , 1 atm	$(7.5 \pm 0.9) \times 10^{-19}$	[30]
	Air, 1 atm	$(6.4 \pm 2.3) \times 10^{-19}$	[31]
	N ₂ , 1 atm	$(6.2 \pm 1.1) \times 10^{-19}$	[32]
	Air, 1 atm	$(7.4 \pm 0.5) \times 10^{-19}$	[33]
$Hg^0_{(g)} + OH_{(g)} \rightarrow HgOH_{(g)}$	Air, 1 atm	$(8.7 \pm 2.8) \times 10^{-14}$	[34]
$HgOH_{(g)} + O_{2(g)} \rightarrow HgO_{(s)} + OH$	N/A, 1 atm (343 K)	$(1.6 \pm 0.2) \times 10^{-11}$	[35]
	Air, 1 atm	$<1.2 \times 10^{-13}$	[36]
	N/A, 1 atm (180–400 K)	$3.2 \times 10^{-13}(T/298K)^{-3.06}$	[18]
	N/A, 1 atm (298 K)	3.2×10^{-13}	
	Air/N ₂ , 1 atm	$(9.0 \pm 1.3) \times 10^{-14}$	[37]
$Hg^0_{(g)} + F_{(g)} \rightarrow HgF_{(g)}$	N/A, 1 atm	$0.92 \times 10^{-12} \exp(206.81/T)$	[2]
	N/A, 1 atm	1.86×10^{-12}	
$Hg^0_{(g)} + I_{(g)} \rightarrow HgI_{(g)}$	N/A, 1 atm (180–400 K)	$4.0 \times 10^{-13}(T/298 K)^{-2.38}$	[18]
	N/A, 1 atm (298 K)	4.0×10^{-13}	
$Hg^0_{(g)} + Cl_{2(g)} \rightarrow HgCl_{2(g)}$	Air, N ₂ , 1 atm	$(2.6 \pm 0.2) \times 10^{-18}$	[16]
	Air, 1 atm	$(2.5 \pm 0.9) \times 10^{-18}$	[31]
	N ₂ , 1 atm	4.3×10^{-15}	[25]
$Hg^0_{(g)} + Br_{2(g)} \rightarrow HgBr_{2(g)}$	Air, N ₂ , 1 atm	$<(0.9 \pm 0.2) \times 10^{-16}$	[16]
$Hg^0_{(g)} + F_{2(g)} \rightarrow Hg^{2+} + Products$	Air, 1 atm	$(1.8 \pm 0.4) \times 10^{-15}$	[31]
	N ₂ , 1 atm	$\leq (1.27 \pm 0.58) \times 10^{-19}$	[38]
$Hg^0_{(g)} + ClO_{(g)} \rightarrow HgClO_{(g)}$	N ₂ , 1 atm	1.1×10^{-11}	[25]
$Hg^0_{(g)} + BrO_{(g)} \rightarrow HgBrO_{(g)}$	Air, NO, 1 atm	$(3.0-6.4) \times 10^{-14}$	[17]
	N ₂ , 1 atm	$(1-100) \times 10^{-15}$	[39]
$Hg^0_{(g)} + NO_{3(g)} \rightarrow HgO_{(g)} + NO_{2(g)}$	N ₂ , (5–10) × 10 ⁻³ atm	$<4 \times 10^{-15}$	[34]
	Air, 1 atm	$<7 \times 10^{-15}$	[31]

$Hg^0_{(g)} + H_2O_{2(g)} \rightarrow HgO_{(g)} + H_2O_{(g)}$	N/A, 1 atm	$\leq 4.1 \times 10^{-16}$	[40]
	N ₂ , N/A	$< 8.5 \times 10^{-19}$	[41]

^a. Room Temperature, unless noted otherwise; ^b. The unit is cm³ molec⁻¹ s⁻¹ unless noted otherwise.

2.1. Br-initiated Oxidation of Hg^0

Oxidation of Hg^0 by Br occurs via a two-step process with $HgBr$ as the intermediate. Previous quantum calculations by Dibble, et al. [42] demonstrated that $BrHg$ could react with the abundant radicals in the atmosphere to form the stable compounds $BrHgY$ —where Y is NO_2 , HO_2 , ClO , or BrO . Previous laboratory studies reported the apparent rate coefficients in the range of $(3.6 \pm 0.9) \times 10^{-13}$ to $(3.2 \pm 0.3) \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$, at 1 atm and 298 K [16,17,19]. Theoretical studies estimated the rate constants to be from 9.8×10^{-13} to $2.1 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$, at 1 atm and 298 K [2,18,20]. Theoretical and experimental rate constants for mercury oxidation by Br and Cl atoms at 298 K have previously been compared in detail in Table A.2 by Subir et al. [15].

The first kinetic study of the reactions of $BrHg$ with the atmospherically abundant radicals NO_2 and HO_2 was recently reported by Jiao and Dibble [43], using computational chemistry. The reactants, products and well-defined transition states were characterized using the coupled cluster singles, doubles, and non-iterative triples (CCSD(T)) with large basis sets. The potential energy profiles for the barrierless addition of HO_2 and NO_2 to $BrHg$ were characterized using Multireference second-order perturbation theory (CASPT2) and the full coupled cluster single, double, and triple excitations method based on a spin-restricted Hartree–Fock wavefunction (RHF-CCSDT) and the rate constants were computed as a function of temperature and pressure using variational transition state theory and master equation simulations. $Syn-BrHgONO$ was effectively the sole product of the addition of NO_2 to $BrHg$ (oxidation) under atmospheric conditions due to its thermodynamic stability and the kinetic instability of $BrHgNO_2$ and anti- $BrHgONO$. The rate constant for oxidation by NO_2 was roughly twice that for oxidation by HO_2 in the temperature range 200–320 K. Since the concentration ratio of $[NO_2]$ to $[HO_2]$ is highly variable, the fate of $BrHg$ depends more on the ratio of $[NO_2]$ to $[HO_2]$ than on the ratio of rate constants. A previously unsuspected reaction channel for $BrHg + NO_2$ competed with the addition to yield $Hg + BrNO_2$. This reaction reduced the mercury oxidation state in $BrHg$ from Hg^I to Hg^0 and slowed the atmospheric oxidation of Hg^0 . While the rate constant for this reduction channel was not well-constrained by the present calculations, it may be as much as 18% as large as the oxidation channel under some atmospheric conditions. The rate constants computed in this study not only provided a quantitative description of the mechanism of atmospheric mercury oxidation but also gave a starting point for experimentalists planning to investigate the atmospheric chemistry of mercury initiated by bromine.

Sun et al. [21] used a relative rate technique and determined the rate coefficients for $Hg^0 + Br\bullet$ reactions to be $(1.6 \pm 0.8) \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$, at 100 kPa and 298 ± 3 K. In this study, the Br atoms were produced in-situ via intermittent photolysis of $CHBr_3$ and light hydrocarbons (ethane and propene for $Br\bullet$ reactions) were selected as references to reduce possible secondary reactions. The effects of wall deposits were minimized by always using newly conditioned 160 L collapsible FEP Teflon-film chambers (Polymer Institute of Shanghai, China) for consecutive runs. The determined rate coefficient was in the midst of previously reported rate constants. Measurements using a scanning mobility particle sizer by Sun, Sommar, Feng, Lin, Ge, Wang, Yin, Fu and Shang [21] also revealed that a large portion of Hg products existing as wall deposits. It's been suggested that the presence of aerosols in the Aitken mode during the oxidation reaction may originate from vapor nucleation of mercury-containing products followed by the growth and condensation of vapor constituents. The product analysis agreed with the previous study by Ariya, Khalizov and Gidas [16].

2.2. Cl-initiated Oxidation of Hg^0

Similar as Hg^0 -Br oxidation, the Hg^0 -Cl reaction was believed to occur via a two-step chlorination process with $HgCl_2$ as the primary identified product [16,21,24]. Theoretical calculations indicated that after the initializing step to form $HgCl$ intermediate, the secondary oxidation of $HgCl$ could be carried out by NO_2 , HO_2 , ClO , or BrO . Recently, Sun, Sommar, Feng, Lin, Ge, Wang, Yin, Fu and Shang [21] determined the rate coefficients using a relative rate technique with ethane and 2-chloropropane as references. The Cl atoms were produced in-situ via intermittent photolysis of precursors $CCl_3C(O)Cl$. Photolysis experiments were performed using 160 L collapsible FEP Teflon-film

chambers equipped with a valve for filling reaction mixtures and collecting samples. The rate coefficient for the $\text{Hg}^0 + \text{Cl} \bullet$ reaction was reported to be $(1.8 \pm 0.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, at 100 kPa and $298 \pm 3 \text{ K}$, which was in agreement with three earlier laboratory studies by Horne, et al. [23], Spicer, Satola, Abbgly, Plastridge and Cowen [17] and Ariya, Khalizov and Gidas [16] ($1.0\text{--}8.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). However, the reported rate coefficient was about two orders of magnitude larger than that determined by Donohoue, Bauer and Hynes [24] ($5.4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and one order of magnitude smaller than that determined by Byun, et al. [25] ($1.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). The determined rate constant was one order of magnitude higher than the only theoretical estimation by Khalizov et al. (2003) [2] ($2.81 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). More studies are needed to reduce the uncertainties in kinetic estimate. To render it more complex, as the existing reactions shows the importance of surfaces in catalysis and heterogeneous reactions [3,44], further studies on atmospheric relevant surfaces and particles are recommended.

2.3. Oxidation of Hg^0 by NO_3

Nitrate radical (NO_3) is a nighttime oxidant generated mainly from the reaction of O_3 and nitrogen dioxide (NO_2) [45]. The experimentally determined rate constant for this oxidation pathway has been previously reported to be $<4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ by Sommar, et al. [34] and $<7 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ by Sumner, et al. [31] at 1 atm and 298 K. Yet, on the basis of the new HgO thermochemistry, Hynes et al. (2009) estimated the reaction to be endothermic of 195 kJ/mol and thus, suggested this oxidation pathway not important in the atmosphere. Furthermore, theoretical calculations by Dibble, Zelig and Mao [42] suggest that NO_3 do not form strong bonds with Hg^0 and thus cannot initiate Hg^0 oxidation in the gas phase.

A recent field study by Peleg, et al. [46] provided the certain observational evidence for involvement of nitrate radicals in nighttime oxidation of mercury. In their study, continuous measurements of atmospheric nitrate radical (NO_3) concentrations and mercury speciation (i.e. Hg^0 and Hg^{II}) were performed during a six-week period in the urban air shed of Jerusalem, Israel during summer 2012 to investigate the potential nighttime contribution of nitrate radicals to oxidized mercury formation. A strong correlation was observed between nighttime Hg^{II} concentrations and nitrate radical concentration (R^2 averaging 0.47), while correlations to other variables were weak (e.g., RH: Relative Humidity; $R^2= 0.35$) or absent (e.g., ozone, wind speed and direction, pollution tracers such as CO or SO_2). Their observations suggest that NO_3 radicals may play a role in Hg^{II} formation, possibly due to a direct chemical involvement in Hg^0 oxidation. Since previous theoretical calculations suggested that NO_3 may be unlikely to initiate Hg^0 oxidation [42,47], NO_3 may play a secondary role in Hg^0 oxidation through the addition to an unstable Hg^{I} radical species. More laboratory and theoretical studies are required to assess the role of NO_3 in secondary reactions of Hg^0 oxidation in the real atmosphere, including on atmospheric relevant surfaces.

2.4. Dominant Gaseous Oxidant for Hg^0 : O_3/OH , Br or Others?

Previous work assumed gas-phase OH and ozone to be the dominant Hg^0 oxidants [48–53]. Some thermodynamic studies suggested that the corresponding gaseous HgOH and HgO products may be too thermally unstable to enable oxidation to Hg^{II} under atmospheric conditions [18,47,54,55]. In spite of theoretical doubts about the viability and significance of direct homogeneous gas-phase Hg^0 oxidation by ozone (O_3) and hydroxyl radical (OH) under atmospheric conditions, numerous modeling studies using these reactions as the main Hg oxidation pathways in the free troposphere also demonstrated reasonable results compared with observed Hg^0 concentration and wet deposition flux [51,53,56–60]. Besides, both theoretical and laboratory studies suggest that complex Hg oxidation mechanisms, particularly heterogeneous reactions involving O_3 and OH, may exist in the atmosphere in the presence of aerosol particles and secondary reactants [3,32,33,44,61].

Reactive halogens are important oxidants of Hg^0 in the marine boundary layer and in the Arctic, where Br is found to be the most dominant oxidant. The lifetime of Hg^0 can be as short as a few hours to a few days when the air is enriched with Br [62–64]. Owing to the chemical uncertainties associated with O_3 and OH, Holmes, et al. [65] conducted a global modeling study using Br as the primary

gaseous oxidant, concluding that Br is a major sink and could be the dominant oxidant of Hg^0 in the atmosphere globally. The presence of BrO radical has been recently observed in the upper troposphere [66,67] as well as over the southeastern US [4,68]. Because the rapid exchange between Br and BrO radicals [69] and much slower oxidation rate of Hg^0 by BrO [15], the field observations of BrO are consistent with Br atoms acting as the main Hg^0 oxidant in the atmosphere. Shah et al. 2016 [4] found that sensitivity simulations using the GEOS-Chem chemical transport model with tripled bromine radical concentrations, or a faster oxidation rate constant for $\text{Hg}^0 + \text{Br}$, resulted in 1.5–2 times higher modeled Hg^{II} concentrations and improved agreement with the aircraft observations. Note that there is significant variability in the temporal and spatial variation of its concentration and distribution, which should be considered when assessing its impact as a global oxidant, particularly as oxidized mercury is observed in the upper troposphere in the absence of elevated BrO concentrations [12]. Yet, the consistent BrO measurements do not exist in the lower troposphere where humans and biota exist. Moreover, note that the majority of chemical compounds are more concentrated and diversified in the boundary layer, which leads to much more complexity in chemistry, physics and biology due to various interfacial processes. The field studies by Mae Gustin and co-workers during the last decades also suggested that the oxidized mercury may be due to the oxidation of Hg^0 not just by Br or BrO but various oxidants. The composition of oxidized mercury showed that Hg^0 is subject to the oxidation processes with various oxidants and not necessarily Br. The assumption of the universality of Br oxidation as a global oxidant may need further evaluation [70].

Most recent modeling studies indicated more complex Hg chemistry in the atmosphere and multiple oxidants may be significant under various atmospheric conditions. Ye, et al. [71] developed a box model incorporating a state-of-the-art chemical mechanism for atmospheric mercury (Hg) cycling to investigate the oxidation of Hg^0 at three locations in the northeastern United States: Appledore Island (AI; marine), Thompson Farm (TF; coastal, rural) and Pack Monadnock (PM; inland, rural, elevated). The chemical mechanism in this box model included the most up-to-date Hg and halogen chemistry. As a result, the box model was able to simulate reasonably the observed diurnal cycles of Hg^{II} and chemical speciation bearing distinct differences between the three sites. In agreement with observations, simulated Hg^{II} diurnal cycles at AI and TF showed significant daytime peaks in the afternoon and nighttime minimums compared to flat Hg^{II} diurnal cycles at PM. Moreover, significant differences in the magnitude of Hg^{II} diurnal amplitude (AI > TF > PM) were captured in modeled results. At the coastal and inland sites, Hg^0 oxidation was predominated by O_3 and OH, contributing 80–99% of total Hg^{II} production during daytime. H_2O_2 -initiated Hg^0 oxidation was significant (33% of the total Hg^{II}) at the inland site during nighttime. In the marine boundary layer (MBL) atmosphere, Br and BrO became dominant Hg^0 oxidants, with mixing ratios reaching 0.1 and 1 pptv respectively, and contributing ~70% of the total Hg^{II} production during midday, while O_3 dominated Hg^0 oxidation (50–90% of Hg^{II} production) over the remainder of the day when Br and BrO mixing ratios were diminished. The majority of HgBr produced from $\text{Hg}^0 + \text{Br}$ was oxidized by NO_2 and HO_2 to form brominated Hg^{II} species. In Br chemistry, the products of the $\text{CH}_3\text{O}_2 + \text{BrO}$ reaction strongly influenced the simulated Br and Hg concentrations.

Travnikov, et al. [72] provided a complex analysis of processes governing Hg fate in the atmosphere involving both measured data from ground-based sites and simulation results from chemical transport models. A variety of long-term measurements of Hg^0 and Hg^{II} concentrations as well as Hg wet deposition flux have been compiled from different global and regional monitoring networks. Four contemporary global-scale transport models for Hg were used, both in their state-of-the-art configurations and for a number of numerical experiments to evaluate particular processes. Results of the model simulations were evaluated against measurements. Results indicated that air concentration of Hg^{II} and wet deposition are largely defined by oxidation chemistry. The Br oxidation mechanism can reproduce successfully the observed seasonal variation of the $\text{Hg}^{\text{II}}/\text{Hg}^0$ ratio in the near-surface layer but it predicted a wet deposition maximum in spring instead of in summer as observed at monitoring sites in North America and Europe. Model ran with OH chemistry correctly simulate both the periods of maximum and minimum values and the amplitude of observed seasonal

variation but shifted the maximum $\text{Hg}^{\text{II}}/\text{Hg}^0$ ratios from spring to summer. O_3 chemistry did not predict significant seasonal variation of Hg oxidation. Hence, the performance of the Hg oxidation mechanisms studied differed in the quality of their reproduction of the various observed parameters, which can imply the possibility of more complex chemistry and multiple Hg oxidation pathways initiated by Br or O_3/OH or OH occurring concurrently in various parts of the atmosphere.

Gencarelli, et al. [73] simulated the deposition, transport and chemical interactions of atmospheric Hg over Europe for the year 2013 in the framework of the Global Mercury Observation System (GMOS) project. The outputs of 14 model sensitivity tests were compared between themselves and with available measurements from 28 monitoring sites. In general, good agreement between the model and observations was found, especially in the stations bordering the Baltic and Mediterranean seas. Using a reaction mechanism with Hg^0 oxidation by only O_3 or OH greatly underestimates the observed deposition in precipitation. Whereas using a mechanism with Br as the Hg^0 oxidant produced more Hg^{II} at ground level, the overall Hg wet deposition is lower than the simulation employing both O_3 and OH in the oxidation mechanism. These model results indicated that the oxidation of Hg^0 by either O_3 , OH or Br alone cannot provide a good prediction of Hg deposition, which indicated a more complex oxidation mechanism.

Bieser, et al. [74] performed a model intercomparison study investigating the impact of atmospheric chemistry and emissions on mercury in the atmosphere. The vertical and interhemispheric distribution and speciation of mercury was investigated from the planetary boundary layer to the lower stratosphere. The first comprehensive analysis was presented based on various aircraft observations in Europe, North America and on intercontinental flights. The investigated models proved to be able to reproduce the distribution of total and elemental mercury concentrations in the troposphere including interhemispheric trends. One key aspect of the study is the investigation of mercury oxidation in the troposphere. It was found that different chemistry schemes were better at reproducing observed Hg^{II} patterns depending on altitude. High concentrations of Hg^{II} in the upper troposphere could be reproduced with oxidation by bromine while elevated concentrations in the lower troposphere were better reproduced by OH and ozone chemistry. However, the results were not always conclusive as the physical and chemical parameterizations in the chemistry transport models also proved to have a substantial impact on model results.

Recent model studies seemed to suggest that multiple oxidants are likely involved in the oxidation of atmospheric Hg^0 dependent on seasons and locations. However, whether Br, O_3/OH or multiple oxidants are the major oxidants of Hg^0 in the global atmosphere is unclear. To address this important question, more studies on reducing the large uncertainties in rate constants, understanding the heterogeneous Hg^0 oxidation by O_3/OH , improving the treatment of chemical mechanisms in chemical transport models and the accuracy of mercury emission inventories are needed.

3. Chemical Redox Reactions of Hg in the Aqueous Phase

To date, the proposed chemical oxidation pathways in atmospheric droplets include the aqueous oxidation of Hg^0 by O_3 , OH, chlorine (HOCl/OCl^-) and bromine ($\text{Br}_2/\text{HOBr}/\text{BrO}^-$). The proposed chemical reduction pathways of mercury in the aqueous phase relevant to natural conditions include reduction of Hg^{II} by sulfite, photo-reduction of $\text{Hg}(\text{OH})_2$, photo-reduction of Hg^{II} by HO_2 and photo-reduction of Hg^{II} -dicarboxylic acid complexes. The obtained rate constants and proposed mechanisms for these reactions were summarized in Table 2. Recent advances include the aqueous photoreduction of Hg^{II} -organic complexes and the effects of environmental variables on the aqueous reduction of Hg^{II} by sulfite.

Table 2. Current Accumulated Knowledge on Chemical Redox Pathways of Hg in the Aqueous Phase.

Reactant (s)	Rate Constants	T (K)	pH	Potential mechanism	Reference	
Identified Reduction Pathways of Hg ²⁺						
Hg ²⁺ + sulfite (aq)	0.6 s ⁻¹	299	3	$HgSO_3 \rightarrow Hg^+ \xrightarrow{+HSO_3^- \text{ or } +Hg^+} Hg^0 + \text{products}$	[75]	
	0.0106 ± 0.0009 s ⁻¹	298	3	$HgSO_3 + nH_2O \rightarrow [Hg(SO_3) \cdot (H_2O)_n] \rightarrow Hg^0 + \text{products}$	[76]	
	0.013 ± 0.007 s ⁻¹	298	7	Same as above	[77]	
Hg(OH) ₂	3 × 10 ⁻⁷ s ⁻¹	293	7	$Hg(OH)_2 \xrightarrow{h\nu} [Hg(OH)_2^*] \rightarrow Hg(OH)^\bullet + \bullet OH$	[78]	
HgS ₂ ²⁻	~10 ⁻⁷ s ⁻¹	298		Not available	[78]	
Hg ²⁺ + HO ₂	1.7 × 10 ⁴ M ⁻¹ s ⁻¹	298		$C_2O_4^{2-} + 2O_2 \xrightarrow{h\nu} 2O_2^{\bullet -} + 2CO_2$ $O_2^{\bullet -} + H^+ \rightarrow HO_2^\bullet$ $HO_2^\bullet + Hg^{2+} \rightarrow Hg^+ + O_2 + H^+$ $HO_2^\bullet + Hg^+ \rightarrow Hg^0 + O_2 + H^+$ $HO_2^\bullet + HO_2^\bullet \rightarrow H_2O_2 + O_2$	[79]	
				Not available	Intramolecular 2e ⁻ transfer via Hg ²⁺ -oxalate complex	[80]
Hg ²⁺ +Dicarboxylic acids (C ₂ –C ₄)	(1.2 ± 0.2) × 10 ⁴ M ⁻¹ s ⁻¹ (Oxalic) (4.9 ± 0.8) × 10 ³ M ⁻¹ s ⁻¹ (Malonic); (2.8 ± 0.5) × 10 ³ M ⁻¹ s ⁻¹ (Succinic)		296	3.0	Mainly intramolecular 2e ⁻ transfer via Hg ²⁺ -dicarboxylate complexes	[81]
Identified Aqueous Oxidation Pathways of Hg ⁰						
Hg ⁰ + O ₃	(4.7 ± 2.2) × 10 ⁻⁷ M ⁻¹ s ⁻¹				$Hg^0 + O_3 \longrightarrow HgO + OH^- + O_2$ $HgO + H^+ \longrightarrow Hg^{2+} + OH^-$	[82]

	$2.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	$\text{Hg}^0 + \bullet\text{OH} \rightarrow \text{Hg}^+ + \text{OH}$ $\text{Hg}^+ + \bullet\text{OH} \rightarrow \text{Hg}^{2+} + \text{OH}^-$	[79]
$\text{Hg}^0 + \bullet\text{OH}$	$(2.4 \pm 0.3) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	$\text{Hg}^0 + \bullet\text{OH} \rightarrow \bullet\text{HgOH}$ $\bullet\text{HgOH} + \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Hg}(\text{OH})_2 + \text{H}^+ + \text{O}_2^-$ $\bullet\text{HgOH} + \bullet\text{OH} \rightarrow \text{Hg}(\text{OH})_2$	[83]
	$5.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	$2 \bullet\text{HgOH} \rightarrow \text{Hg}_2(\text{OH})_2 \leftrightarrow \text{Hg}^0 + \text{Hg}(\text{OH})_2$	[84]
		Not available	[84]
$\text{Hg}^0 + \text{HOCl}/\text{OCl}^-$	$(2.09 \pm 0.06) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$	$\text{HOCl} + \text{Hg}^0 \rightarrow \text{Hg}^{2+} + \text{Cl}^- + \text{OH}^-$	[85]
	$(1.99 \pm 0.05) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$	$\text{OCl}^- + \text{Hg}^0 \xrightarrow{\text{H}^+} \text{Hg}^{2+} + \text{Cl}^- + \text{OH}^-$	

3.1. Field Evidence for the Reduction of Hg^{II}

The reduction reaction of Hg^{II} has been observed in laboratory studies but has not been previously observed via atmospheric observations away from sources. The first field observations of the reduction of Hg^{II} in the presence of sunlight in the atmosphere was recently reported by Foy, et al. [86]. In their study, hourly speciated measurements of atmospheric mercury were made in a remote, high-altitude site in the Tibetan Plateau. Measurements were collected over four winter months on the shore of Nam Co. Lake in the inland Tibetan Plateau. The data was analyzed to identify sources and atmospheric transformations of the speciated mercury compounds. The absence of local anthropogenic sources provided a unique opportunity to examine chemical transformations of mercury. An optimization algorithm was used to determine the parameters of a chemical box model that would match the measured Hg^{II} concentrations. The agreement between the modeled and the measured Hg^{II} concentration required the presence of a photolytic reduction reaction previously observed in laboratory studies. This work provided further evidence for the importance of the reduction of reactive mercury in the atmosphere. The reduction reaction will need to be addressed in atmospheric models in order to more accurately represent mercury deposition which is greatly impacted by the oxidation state of atmospheric mercury.

3.2. Photoreduction of Hg^{II}-Organic Complexes

The speciation of atmospheric Hg^{II} is unknown [70,87,88]. Besides forming strong complexes with chloride due to high stability constants of Hg^{II}-chloride complexes, Hg^{II} also strongly binds to organic ligands, including to reduced sulfur complexes and carboxyl groups [79,89–91]. Hg–chloride complexes are relatively resistant to photoreduction [79,92]. However, photoreduction of Hg^{II} bound to dissolved organic carbon (DOC) and other organic matter has been widely reported in aquatic environments [93–97] and could also possibly take place in organic aerosols (OA).

Recent model studies provided experimental evidence to support the occurrence of the reduction of Hg^{II}-organic complexes in the atmosphere. Horowitz, et al. [98] implemented the updated chemical mechanism for atmospheric Hg⁰-Hg^{II} redox reactions in the GEOS-Chem global model and examined the implications for the global atmospheric Hg budget and deposition patterns. It was found that implementation of the reduction in GEOS-Chem as photolysis of aqueous-phase Hg^{II}-organic complexes in aerosols and clouds based on previous study by Si and Ariya [81], resulting in a Hg⁰ lifetime of 5.2 months against deposition and matching both mean observed Hg⁰ and its variability. The model reproduces the observed seasonal Hg⁰ variation at northern midlatitudes (maximum in February, minimum in September) driven by chemistry and oceanic evasion but it does not reproduce the lack of seasonality observed at southern hemispheric marine sites. The relatively low observed Hg wet deposition over rural China is attributed to fast Hg^{II} reduction in the presence of high organic aerosol concentrations. Results indicate that 80% of Hg^{II} deposition is to the global oceans, reflecting the marine origin of Br and low concentrations of organic aerosols for Hg^{II} reduction.

3.3. Direct Reduction of Hg^{II} by Sulfite

Sulfite can be formed by the scavenging of SO₂ into atmospheric droplets and thus, the aqueous phase reduction of Hg²⁺ with sulfite is a process relevant to cloud- and rain-water. The first-order rate constant determined by van Loon and her co-workers [76] was widely used in current atmospheric models. To obtain further insights on observed Hg^{II} homogeneous reduction rates by sulfite, the effects of several environmental variables were recently investigated by Feinberg, et al. [77]. Hg(NO₃)₂ and HgO were used as the sources of Hg^{II}. Extended pH (1–7) and temperature (1.0–45.0 °C) ranges were studied for the first time. The enthalpies of activation for the HgO reduction were 94 ± 3 kJ mol⁻¹ at pH 1 and 92 ± 4 kJ mol⁻¹ at pH 3, while the entropies were 33 ± 9 J mol⁻¹ K⁻¹ at pH 1 and 30 ± 10 J mol⁻¹ K⁻¹ at pH 3. With an expanded temperature range, the activation parameters of the HgO sulfite reduction at pH 1 and 3 agree fairly well with the previous study. It was determined that increasing

ionic strength, especially with nitrate species, slows down the reaction at pH = 7. There was no statistical difference between the kinetics of $\text{Hg}(\text{NO}_3)_2$ and HgO , which suggested the reduction of Hg^{II} by sulfite may be independent of Hg^{II} species in aqueous phase. The results indicated the possible occurrence of this reduction reaction under various environmental conditions and thus, its universal inclusion in modeling mercury transformation in the atmosphere and industrial stacks.

4. Heterogeneous Redox Reactions of Hg

In the atmosphere, suspended airborne solid and liquid (heterogeneous/multiphase) particles—technically defined as aerosols [99]—provide sufficient surfaces for gas phase atoms and molecules to adsorb, deposit, or collide. Adsorption of gaseous mercury species can occur on atmospheric surfaces and subsequently they can desorb, undergo surface enhanced (photo) chemical reactions or diffuse to the aqueous compartment where they can exhibit heterogeneous reactions [44]. Despite direct and indirect evidence suggesting that heterogeneous surfaces potentially play a key role in mercury chemistry [32,100], there is little known about mercury reactions and equilibrium processes that take place at atmospherically relevant surfaces. The lack of knowledge on mercury surface chemistry is a major gap for adequate modeling of mercury cycling [3]. The concentration, composition and size distribution of atmospheric aerosol particles are temporally and spatially highly variable. In general, the predominant chemical components of air particulate matter (PM) are sulfate, nitrate, ammonium, sea salt, mineral dust, organic compounds and black or elemental carbon, each of which typically contributes about 10–30% of the overall mass load. The varying size distribution (~1 nm to ~20 μm) and composition of aerosols at different locations, times, meteorological conditions and particle size fractions [99,101], make systematic understanding of its surface chemistry challenging [102]. Nevertheless, several recent laboratory studies focus on understanding the complex heterogeneous reactions between atmospheric mercury and various aerosols. The major findings in these studies are summarized in Table 3. Feinberg, Kurien and Ariya [77] used UV absorption spectroscopy to study the kinetics of Hg^{2+} reduction by sulfite (Na_2SO_3) in the presence of fly ash. Compared with the homogeneous reduction rate, the addition of fly ash samples from Cumberland Power Plant (Tennessee) and Shawnee Fossil Plant (Kentucky) reduced the reduction rates by c.a. 45% and 95%, respectively. For the first time, the effect of fly ash on sulfite reduction was evaluated. The reduction reaction was also observed when the fly ash samples from Cumberland Power Plant (Tennessee) were added without Na_2SO_3 . Sulfur elemental analyzer and high-resolution field emission scanning microscopy with energy dispersive X-ray spectroscopy (HR-FE-SEM-EDS) characterization confirmed that fly ash particles from Cumberland Power Plant (Tennessee) were rich in sulfur. The richness of sulfite in these fly ash samples may explain why the reduction of mercury by Cumberland fly ash was independent of whether Na_2SO_3 was added. Nanoparticle Tracking Analysis (NTA) determined the mean particle size in solution to be 246 ± 25 nm for Cumberland fly ash and 198 ± 14 nm for Shawnee. The high proportion of nanoparticles in the fly ash samples suggested that there were a large number of available surfaces for heterogeneous chemistry. These findings impact the current treatment of mercury reduction reactions in models of atmospheric and aqueous systems.

Table 3. Current accumulated Knowledge on Heterogeneous Chemical Reactions of Hg in the Atmosphere.

Reactants	Solid Phase	Major Findings	References
Hg ²⁺ + organic acids	0.1 g/liron oxides particles or 0.01 g/lambient aerosols	The presence of iron oxides or ambient aerosols enhanced the rate. Proposed Mechanism: $\text{Fe}^{3+} - \text{OH} \xrightarrow{+\text{OA}} \text{Fe}^{3+} - \text{OA} \xrightarrow{h\nu} \text{R}^{\bullet} \xrightarrow{+\text{Hg}^{2+}} \text{Hg}^0$	[103]
HgCl ₂	Synthetic NaCl aerosols	Significant reduction of Hg ^{II} observed upon UV, visible or a simulated solar radiation. The presence of iron in synthetic NaCl aerosols inhibited the reduction rate.	[104]
HgCl ₂	Coal fly ash or synthetic aerosols	The average half-life was estimated to be 1.6 h under clear sky atmospheric conditions from the reduction rate on three diverse fly ash samples; The rate on low sulfate/low carbon fly ash was 1.5 times faster than other fly ash samples. The rate on synthetic aerosols of carbon black and levoglucosan similar to coal fly ashes; The presence of adipic acid in synthetic aerosols increased the reduction rate by 3–5 times. The soluble components of fly ash play a significant role in the reduction.	[105]
Hg ²⁺ +sulfite	Fly ash	The presence of Cumberland and Shawnee fly ash samples inhibited the reduction rate. The reduction was observed in Cumberland fly ash without sulfite. Cumberland fly ash was rich in sulfur with mean particle size of 246 ± 25 nm. The mean size of Shawnee fly ash was 198 ± 14 nm.	[77]
HgCl ₂ , HgBr ₂ , Hg(NO ₃) ₂ , HgSO ₄	Fe(110), NaCl(100) and NaCl(111) ^{Na}	The reduction was highly favorable on Fe(110) and NaCl(111) ^{Na} surfaces. An external energy source of ~0.5 eV is required for Fe(110) surfaces to desorb the reduced Hg, whereas no energy input was needed for NaCl(111) ^{Na} surfaces. A number of Hg ^I species can be reduced on metallic iron and NaCl surfaces.	[106]

Previous laboratory studies showed that the heterogeneous reduction reaction of Hg^{II} could occur on iron and sodium chloride aerosol surfaces [104]. Recently, theoretical calculations by Tacey, et al. [106] supported the experimental results. In this study, density functional theory calculations were used to discern the reduction pathways of HgCl_2 , HgBr_2 , $\text{Hg}(\text{NO}_3)_2$ and HgSO_4 on clean $\text{Fe}(110)$, $\text{NaCl}(100)$ and $\text{NaCl}(111)^{\text{Na}}$ surfaces. Here, $\text{Fe}(110)$ is the most thermodynamically stable facet of iron and therefore the most abundant surface on metallic iron aerosols. The $\text{NaCl}(100)$ facet is comprised of neutrally charged layers, exposing both Na and Cl atoms on the surface, whereas $\text{NaCl}(111)^{\text{Na}}$ surfaces are charged layers that expose solely Na atoms. Potential energy surfaces were prepared for the various reduction pathways, indicating that the reduction pathway leading to the production of gas-phase elemental mercury is highly favorable on $\text{Fe}(110)$ and $\text{NaCl}(111)^{\text{Na}}$. Moreover, the $\text{Fe}(110)$ surface required an external energy source of ~ 0.5 eV to desorb the reduced mercury, whereas the $\text{NaCl}(111)^{\text{Na}}$ surface required no energy input. The results indicate that a number of mercury species can be reduced on metallic iron and sodium chloride surfaces, which are known aerosol components and that a photochemical reaction involving the aerosol surface is likely needed for the reaction to be catalytic.

Kurien, et al. [107] have provided systematic studies on understanding the heterogeneous chemistry of mercury, specifically on ubiquitous dust particle surfaces in the environment. They provided the uptake coefficients for the uptake of $\text{Hg}^0(\text{g})$ on iron(oxyhydr)oxides ($\gamma\text{-Fe}_2\text{O}_3$, $\alpha\text{-FeOOH}$, $\alpha\text{-Fe}_2\text{O}_3$ and Fe_3O_4) nanoparticles, employed as proxies for reactive components of mineral dust. $\text{Hg}^0(\text{g})$ -particle interactions have also been studied in a batch set-up, at ambient pressure (~ 760 Torr) and temperatures (~ 295 K) with UV and visible irradiation (290 nm to 700 nm). $\gamma\text{-Fe}_2\text{O}_3$, $\alpha\text{-FeOOH}$ and $\alpha\text{-Fe}_2\text{O}_3$ demonstrated a ca. 40–900-fold increase in uptake kinetics upon irradiation, under experimental conditions. In contrast, uptake kinetics on Fe_3O_4 's surface displayed little dependence on irradiation. Relative humidity was shown to inhibit the effect of radiation on the uptake of $\text{Hg}^0(\text{g})$ by $\alpha\text{-Fe}_2\text{O}_3$. The difference in uptake behavior of the iron (oxyhydr)oxides were attributed to their band gaps and consequently the redox potentials of the electron–hole pairs. These uptake reactions can potentially increase the number of chemical pathways available for the formation of $\text{Hg}_{(\text{p})}$ and deposition of $\text{Hg}^0(\text{g})$, however, further studies are required to identify and characterize such reactions. Such research presents the need for further studies of heterogeneous chemistry of mercury as elemental mercury and many types of oxidized mercury are likely adsorbed and undergo (photo)chemical reactions in presence of abundant atmospheric surfaces such as particles and clouds.

5. Future Research Directions

Given the relatively high concentration of ozone and the reactivity of OH, as well as their ubiquitous presence in the atmosphere, it is plausible that their oxidation reactions play an important role in $\text{Hg}^0(\text{g})$ oxidation. Large uncertainties exist in current gas-phase reaction rate constants and more studies need to be done to reduce these uncertainties in the first place. More studies are needed to evaluate the contribution of heterogeneous processes to the obtained rate coefficients for the oxidation of Hg^0 by O_3 and/or OH, in order to fully understand the discrepancy between the consistent experimental values and theoretical studies. Secondly, recent theoretical studies indicated that oxidation of Hg^0 could be initiated by Br- or Cl-atoms and then the secondary oxidation of HgX ($\text{X} = \text{Br}$ or Cl) intermediate could be carried out by NO_2 , HO_2 , ClO , or BrO . More laboratory studies are welcome to confirm this oxidation mechanism. Future field work and model sensitivity studies will also provide valuable insights on the viability of these reactions in the atmosphere. Also, more studies supported the significant role of Br in the oxidation of Hg^0 in the atmosphere. Therefore, more kinetic and mechanistic studies are required to reduce the discrepancy in the reported rate constants for the oxidation of Hg^0 by halogen atoms.

Recent model studies seemed to suggest that multiple oxidants are likely involved in the oxidation of atmospheric Hg^0 dependent on seasons and locations. However, whether Br, O_3/OH or multiple oxidants are the major oxidants of Hg^0 in the global atmosphere is unclear. Accurate measurements of vertical tropospheric concentration profiles of the species involved, such as Br, BrO ,

Cl, Hg⁰ (g) as well as detailed chemical composition of oxidized mercury using diverse techniques, are critical for verifying the significance of various oxidants in Hg removal in the atmosphere globally.

Recent field observations and model studies supported the occurrence of reduction reactions in the atmosphere. Furthermore, their results supported the hypothesis that the reduction of Hg^{II}-organic complexes may play an important role in atmospheric Hg cycling besides sulfite-mediated reduction and photo-reduction of Hg(OH)₂. More kinetic and mechanistic studies of Hg^{II} reduction in natural waters and atmospheric droplets especially the reductants responsible for Hg^{II} reduction under realistic environmental conditions are needed. A better understanding of the reduction of Hg^{II} by organic compounds will require both studies on the possible reduction pathways as well as quantification of various organic compounds in the aqueous phase particularly in atmospheric droplets and aerosols.

Another significant knowledge gap is the understanding of the redox transformations that occur on surfaces and in the heterogeneous phase (e.g., water, soil, snow and vegetative surfaces as well as in aerosol). Despite the experimental difficulties caused by the variability in the size and composition of aerosols, several recent studies using fly ash or model aerosols have provided valuable information on understanding heterogeneous reactions on aerosols. The measured reaction rates are likely important in the chemical transformation of mercury in the atmosphere and incorporation of these recent laboratory data in future model studies are essential for reducing uncertainties in current atmospheric Hg models. Such endeavors will benefit from the identification and quantification of oxidized mercury compounds, which has been major challenge in the modeling research. There are novel instruments including mercury mass spectrometry [108], which can be used to provide such information. Further complementary analytical innovations to accurately quantify mercury containing compounds in the atmosphere and atmospheric interfaces are needed.

In the light of the Minamata convention, we encourage a more integrated multi-disciplinary approach to comprehend mercury transformation, dynamic, speciation and remediation. Such integration is required to translate sound science to sound policy and regulations.

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