

Deliverable 2.2.2: Revised reaction mechanisms and rates of atmospheric Hg redox transformations in the Arctic

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Summary

Anthropogenic mercury (Hg(0)) emissions oxidize to gaseous Hg(II) compounds, before deposition to Earth surface ecosystems. Atmospheric reduction of Hg(II) competes with deposition, thereby modifying the magnitude and pattern of Hg deposition. Global Hg chemistry and transport models have postulated that Hg(II) reduction in the atmosphere occurs through aqueous-phase photoreduction that may take place in clouds. Here we report that experimental rainfall Hg(II) photoreduction rates are much slower than modeled rates (Yang et al., 2019). We compute novel absorption cross sections of gaseous Hg(II) compounds and show that fast Hg(II) photolysis in the gas phase can dominate atmospheric mercury reduction (Saiz-Lopez et al., 2018). These results call for a reassessment of Arctic and global atmospheric Hg cycling.

Laboratory rainfall Hg(II) photoreduction experiments

To study aqueous phase Hg(II) photoreduction, ten rainfall events were sampled in sub-urban Toulouse and at the high altitude (2877m) Pic du Midi Observatory (PDM, France) in the summer of 2017. Details can be found in (Saiz-Lopez et al., 2018; Yang et al., 2019). Rainfall samples were irradiated in a quartz reactor with natural sunlight or with a solar simulator. We observe no statistically significant differences between rainfall Hg(II) reduction rates under natural (0.063 ± 0.013 h-1) and simulated sunlight (0.037



 \pm 0.016 h-1), and for filtered (0.058 \pm 0.011 h-1) and unfiltered (0.039 \pm 0.020 h-1) suburban rainwater (t-test, all p>0.05). The mean photochemical reduction rate of suburban rainfall was 0.08 \pm 0.05 h-1 (σ , n=10). The mean rate at the remote PDM samples was two-fold higher, 0.15 \pm 0.01 h-1 (σ , n=3), than that of the suburban Toulouse samples, and three times slower than the median photoreduction rate of 0.41 h-1 (n=24) for inland and marine waters. Our experimental rainwater photoreduction rates, under fully sunlit conditions, are an order of magnitude slower that the optimized maximum in-cloud photoreduction rate in global Hg CTMs (Horowitz et al., 2017; Selin et al., 2007) of >1.0 h-1.

Quantum chemical computation of gaseous Hg(II) absorption cross sections.

We now turn to the computation of electronic spectra and absorption cross sections of gas-phase Hg(II) compounds which are required to estimate the corresponding photoreduction rates. A summary of the novel UV-VIS spectra and absorption cross sections, computed at the CASSCF/MS–CASPT2/SO–RASSI level of theory (Methods), is presented in Figure 1 of Saiz-Lopez et al. (2018) for the 170 to 600 nm wavelength range. The majority of the spectra consist of well-defined absorption bands in the 200-350 nm range, which are red-shifted when Cl is replaced with Br and I atoms. Note that three different isomers could form from the reaction of HgBr with NO2: HgBrNO2, and syn- and anti-HgBrONO. However, high-level quantum chemical computations indicate that syn-HgBrONO is the most thermodynamically stable species.

The absorption cross sections of syn-HgBrONO, HgBrOOH, HgBrOH, HgBr2, HgBrOCl and HgBrOBr were implemented into the GEOS-Chem and GLEMOS global Hg chemistry and transport models (Saiz-Lopez et al., 2018), since these Hg(II) species are the most likely to be formed in the atmosphere. The updated atmospheric Hg redox mechanism for both models are given in Table 1, and Figure 1. GEOS-Chem simulates Hg(II) as a single tracer, whereas GLEMOS simulates Hg(II) species individually. Atmospheric aqueous Hg(II) reduction parameterizations in both models were capped with an upper limit that corresponds to our observed rainfall photoreduction rate constant, $k_{red} = 0.15$ (h-1). Published model runs with fast aqueous phase Hg(II) reduction and without the gas-phase photoreduction yield total atmospheric Hg lifetimes of 5.2 and 4.6 months against deposition. Our new results show that gaseous



Hg(II) photoreduction increases the Hg lifetime to 8 and 10 months in GEOS-Chem and GLEMOS models respectively. We find that gas-phase photoreduction is the dominant reduction pathway.

This work shows that the presence of an efficient gaseous phase Hg(II) photoreduction challenges our understanding of Hg cycling in the atmosphere and its deposition to the surface environment. We show that the new gas-phase Hg(II) photoreduction mechanism is likely the dominant reduction pathway for atmospheric mercury which changes the concept of the speciation of Hg(II) in the atmosphere. Its inclusion in state-of-the-art global models leads to significant modifications in the local scale deposition of Hg to the Earth's surface. As a result, enhanced deposition to land surfaces may prolong recovery of aquatic ecosystems long after Hg emissions are curbed, due to the longer residence time of Hg in soils than in oceans. These results call for a reassessment of Arctic and global atmospheric Hg cycling.

N	Reaction GLEMOS	Rate expression
R1	$Hg^0 + Br + M \rightarrow HgBr + M$	$1.5 \times 10^{-32} (T/298)^{-1.86} [Hg^0][Br][M]$
R2	$HgBr + M \rightarrow Hg^0 + Br + M$	1.6 × 10 ⁻⁹ exp(-7801/T) [HgBr][M]
R3	$HgBr + Br \rightarrow Hg^{0} + Br_{2}$	3.9 × 10 ⁻¹¹ [HgBr][Br]
R4	$HgBr + Br \xrightarrow{M} HgBr_2$	2.5 × 10 ⁻¹⁰ (T/298) ^{-0.57} [HgBr][Br]
R5	$HgBr + OH \longrightarrow HgBrOH$	2.5 × 10 ⁻¹⁰ (T/298) ^{-0.57} [HgBr][OH]
R6	$HgBr + NO_2 \xrightarrow{M} HgBrNO_2$	k _{NO2} ([M],T)[HgBr][NO ₂]
R7	$HgBr + HO_2 \xrightarrow{M} HgBrHO_2$	k _{HO2} ([M],T)[HgBr][HO ₂]
R8	$HgBrY \xrightarrow{hv} HgBr + products$,	k _{photo} ([M],T)[HgBrY]
	$Y = Br, OH, NO_2, HO_2$	
R9	$Hg^{II}(aq) + h\nu \to Hg^{0}(aq)$	4.25× 10 ⁻⁵ [HgII] _{aq}

Table 1. Chemical reaction schemes for atmospheric Hg oxidation and reduction used in the GLEMOS globalHg chemistry and transport model.



Table 2. Chemical reaction schemes for atmospheric Hg oxidation and reduction used in the GEOS-Chemglobal Hg chemistry and transport model.

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	Reaction GEOS-Chem	Rate expression
R1	$Hg^0 + Br + M \rightarrow HgBr + M$	$1.46 \times 10^{-32} (T/298)^{-1.86} [Hg^0] [Br] [M]$
R2	$HgBr + M \rightarrow Hg^0 + Br + M$	$1.6 \times 10^{-9} (T/298)^{-1.86} \exp(-7801/T)[HgBr][M]$
R3	$HgBr + Br \rightarrow Hg^0 + Br_2$	$3.9 \times 10^{-11} [HgBr][Br]$
R4	$HgBr + Br \xrightarrow{M} HgBr$	$3.0 \times 10^{-11} [HgBr][Br]$
R5	$HgBr + NO_2 \xrightarrow{M} HgBrNO_2$	$k_{NO_2}([M],T)[HgBr][NO_2]$
R6	$HgBr + Y \xrightarrow{M} HgBrY$	$k_{HO_2}([M],T)[HgBr][Y]$
	$Y = HO_2, ClO, BrO, OH, Br_2$	
R7	$Hg^0 + Cl + M \rightarrow HgCl + M$	$2.2 \times 10^{-22} \exp(680(1/T - 1/298))[Hg^0][C1][M]$
R8	$HgCl + Cl \rightarrow Hg^0 + Cl_2$	$1.20 \times 10^{-11} \exp(-5942/T)$ [HgCl][Cl]
R9	$HgCl + Br \xrightarrow{M} HgBrCl$	$3.0 \times 10^{-11} [HgCl][Br]$
R10	$HgCl + NO_2 \xrightarrow{M} HgClNO_2$	$k_{NO_2}([M],T)[HgBr][NO_2]$
R11	$HgCl + Y \xrightarrow{M} HgClY$	$k_{HO_2}([M],T)[HgBr][Y]$
	$Y = HO_2, ClO, BrO, OH, Br_2$	
R12	$Hg^{0}_{(aq)} + O_{3(aq)} \rightarrow Hg^{II}_{(aq)} + products$	$4.7\times 10^7[Hg^0{}_{(aq)}][O_{3(aq)}]$
R13	$Hg^{0}_{(aq)} + HOCl_{(aq)} \rightarrow Hg^{II}_{(aq)} + OH^{-}_{(aq)} + Cl^{-}_{(aq)}$	$2 \times 10^{6} [Hg^{0}_{(aq)}][HOCl_{(aq)}]$
R14	$Hg^{0}_{(aq)} + OH_{(aq)} \rightarrow Hg^{II}_{(aq)} + products$	$2.0 \times 10^9 [Hg^{0}_{(aq)}][OH_{(aq)}]$
R14	$Hg^{II}(aq) + h\nu \to Hg^{0}(aq)$	4.25× 10 ⁻⁵ [HgII] _{aq}
R15	$HgBrY \xrightarrow{h\nu} HgBr + products$,	k _{photo} ([M],T)[HgBrY]
	$Y = Br, OH, NO_2, HO_2$	





Figure 1. Annually- and globally-averaged photolysis rate, k_{photo} (s-1, corresponding to GLEMOS R8 and GEOS-Chem R15 in Table 1) and lifetime (h) of Hg(II)BrX compounds in the troposphere.

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