Experimental rainwater divalent mercury speciation and photoreduction rates in the presence of halides and organic carbon

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Abstract

Mercury (Hg) photochemical redox reactions control atmospheric Hg lifetime and therefore play an important role in global Hg cycling. Oxidation of Hg(0) to Hg(II) is currently thought to be a Br-initiated two-stage reaction with end-products HgBr₂, HgBrOH, HgBrONO, HgBrOHO. Atmospheric photoreduction of these Hg(II) compounds can take place in both the gas and aqueous phase. Here we present new experimental observations on aqueous Hg(II) photoreduction rates in the presence of dissolved organic carbon and halides and compare the findings to rainfall Hg(II) photoreduction rates. The pseudo first-order, gross photoreduction rate constant, k_{red} , for 0.5 μM Hg(II) in the presence of 0.5 mg L^{-1} of dissolved organic carbon (DOC) is 0.23 h^{-1} , which is similar to the mean k_{red} ($0.15 \pm 0.01 \text{ h}^{-1}$ (σ , $n = 3$)) in high altitude rainfall and at the lower end of the median k_{red} (0.41 h^{-1} , $n=24$) in continental and marine waters. Addition of bromide (Br^-) to experimental Hg(II)-DOC solutions progressively inhibits Hg(II) photoreduction to reach 0.001 h^{-1} at total Br^- of 10 mM. Halide substitution experiments give Hg(II) $\text{X}_n^{(n-2)}$ photoreduction rate constants of 0.016, 0.004 h^{-1} , and < detection limit for $\text{X} = \text{Cl}^-$, Br^- , and I^- respectively and reflect increasing stability of the Hg(II)-halide complex. We calculate equilibrium Hg(II) speciation in urban and high-altitude rainfall using Visual Minteq, which indicates Hg(II)-DOC to be the dominant Hg species. The ensemble of observations suggests that atmospheric gaseous HgBr₂, HgCl₂, HgBrNO₂, HgBrHO₂ forms, scavenged by aqueous aerosols and cloud droplets, are converted to Hg(II)-DOC forms in rainfall due to abundant organic carbon in aerosols and cloud water. Eventual photoreduction of Hg(II)-DOC in aqueous aerosols and clouds is, however, too slow to be relevant in global atmospheric Hg cycling.

1. Introduction

Mercury (Hg) is a ubiquitous heavy metal found throughout the atmosphere, hydrosphere, biosphere, geosphere and anthroposphere (Selin 2009). Neurotoxicity of Hg to humans and wildlife is of global concern due to widespread exposure via seafood consumption (Wolfe et al. 1998). Emission of Hg to the atmospheric boundary layer occurs mainly in the form of gaseous elemental Hg(0), and to a lesser extent (10%) as gaseous oxidized Hg(II) and particle-bound Hg(P) from natural, anthropogenic and re-emitted sources (Schroeder and Munthe 1998, Futsaeter and Wilson 2013; Horowitz et al., 2017). Hg(0) is characterized by its low chemical reactivity and solubility, and long atmospheric lifetime of several months to over a year. Hg(0) is therefore fairly homogeneously distributed throughout the atmosphere, and can be transported far from its emission sources and deposited to remote ecosystems (Horowitz et al. 2017, Jiskra et al. 2018, Saiz-Lopez et al. 2018). Oxidation of Hg(0) results in the formation of gaseous Hg(II) compounds, which are highly soluble, reactive and have a short atmospheric lifetime of days to weeks, and are readily scavenged by aerosols and clouds and returned to the Earth's surface by dry and wet deposition (Ariya et al. 2015, Saiz-Lopez et al. 2018). Atmospheric Hg(II) compounds can also be reduced back to Hg(0) in both the aqueous and gas phase and results in a prolonged lifetime of atmospheric Hg(0) (Munthe et al. 1991, Si and Ariya 2008, Saiz-Lopez et al. 2018). Redox processes of atmospheric Hg(0) and Hg(II) are considered as an important dynamic balance in global atmospheric Hg cycling and have been widely implemented in global atmospheric Hg chemistry and transport models (Shia et al., 1999; Dastoor and Larocque, 2004; Travnikov and Ryaboshapko 2002, Selin et al. 2007, De Simone et al., 2014; Horowitz et al. 2017). Therefore, quantifying the kinetics and identifying the pathways of these reactions is

crucial to better understand transport and deposition of atmospheric Hg to aquatic and terrestrial systems (Bash et al. 2014).

Production of atmospheric Hg(II) compounds is an important process in the atmosphere, as it is dominantly responsible for atmospheric Hg dry and wet deposition (Lin and Pehkonen 1999, Selin et al. 2007). Speciation of atmospheric Hg(II) is poorly understood, and has only identified as HgCl₂ and HgBr₂ in urban and indoor air and as HgCl₂ in power plant plumes (Ernest et al. 2014, Deeds et al. 2015). Previous research has indicated that gas phase oxidation of atmospheric Hg(0) potentially involves various types of oxidants including O₃, OH, HO₂, H₂O₂, NO₃ and halogen species (Dibble et al. 2012, Peleg et al. 2015, Horowitz et al. 2017). Currently main oxidation of Hg(0) to Hg(II) is thought to be a Br-induced two-step reaction: first, Hg(0) is oxidized to Hg(I)Br by atomic bromide. Secondly, the relatively unstable Hg(I)Br is further oxidized to Hg(II) by other atmospheric radicals, such as OH, Br, I, Cl, NO₂, HO₂, BrO, IO and ClO, to produce dominant Hg-halide end products HgBr₂, HgBrOH, HgBrONO, HgBrOHO (Saiz-Lopez et al. 2018). These gaseous oxidized Hg(II) compounds are water soluble and therefore partition efficiently into cloud water and aqueous aerosols in general (Horowitz et al. 2017).

Photoreduction of dissolved Hg(II) bound to inorganic and organic ligands as well as with humic substances in terrestrial and marine aquatic systems has been widely identified as an important emission source of Hg(0) to the atmosphere (Ariya et al. 2015). Compared to direct photolysis of aqueous inorganic Hg complexes, the Hg-humics photoreduction process is considered to be induced by light energy absorption of dissolved humic substances followed by a primary or secondary reaction (Ravichandran 2004, Zhang 2006). The primary reaction is known as ligand to metal charge transfer: first, the dissolved Hg(II)-DOM complex is reduced to

80 reactive and unstable Hg(I), second, the short-lived reactive intermediate Hg(I) quickly reduced
81 to Hg(0) (Zheng and Hintelmann 2009). The secondary reaction has been proposed by Pehkonen
82 and Lin (1998) via a two-step reduction process: first, dissolved Hg(II) is reduced to Hg(I) by
83 $\text{HO}_2^\cdot$, second, Hg(I) is further reduced to Hg(0) by $\text{HO}_2^\cdot$ (Pehkonen and Lin 1998). The Hg
84 photoreduction rates in natural waters are consistent with pseudo-first-order reaction kinetics and
85 have been reported in a wide range of variability of 0.00125 to 2.5 h^{-1} relative to different light
86 irradiation and DOM (Xiao et al. 1995, O'Driscoll et al. 2006, Qureshi et al. 2011).

87 Atmospheric Hg(II) photoreduction to Hg(0) in aqueous aerosols and clouds determines the
88 lifetime of atmospheric Hg against wet deposition. The first global Hg chemistry and transport
89 model (CTM) included Hg(II) reduction in the atmospheric aqueous phase by sulfite (SO_3^{2-}),
90 with k_{red} of 0.6 s^{-1} (2160 h^{-1}) based on experimental work by Munthe et al. (Munthe et al. 1991,
91 Shia et al. 1999). A later study that directly measured the reactant HgSO_3 put into question the
92 previously proposed reduction mechanism and rate constant, reporting k_{red} of 0.0106 s^{-1} (38.2 h^{-1})
93 (Van Loon et al. 2000). Shia et al.'s CTM also included aqueous phase reduction of Hg(II) by
94 hydroperoxyl, HO_2 , radicals, based on Pehkonen and Lin (1998) with 2nd order k_{red} of $1.7 \times 10^4 \text{ M}^{-1}$
95 s^{-1} (Pehkonen and Lin 1998, Shia et al. 1999). This reaction, which proceeds by a Hg(I)
96 intermediate step has been questioned by Gardfeldt and Jonsson based on the rapid oxidation of
97 the Hg(I) form back to Hg(II) (Gardfeldt et al. 2001). These aqueous phase Hg(II) reduction
98 mechanisms have been gradually abandoned in Hg CTMs, to adopt a fitting approach where
99 aqueous phase Hg(II) photoreduction rates are optimized to balance fast Hg(0) oxidation and
100 reproduce global variability in observed Hg(0). (Travnikov and Ryaboshapko 2002, Selin et al.
101 2007, Horowitz et al. 2017). The fitted k_{red} are typically on the order of 1.0 h^{-1} , which
102 corresponds to Hg(II) lifetimes in clouds and aqueous aerosol of ~20 minutes (Selin et al. 2007).

Despite the long history of experimental and model studies on atmospheric aqueous Hg(II) photoreduction, the process has never been directly observed or quantified on natural samples. Recently, we conducted the first aqueous phase photoreduction experiments of Hg(II) in rainfall and observed slow values for k_{red} in sub-urban ($0.05 \pm 0.02 \text{ h}^{-1}$, 1σ , $n=9$) and high-altitude rain ($0.15 \pm 0.01 \text{ h}^{-1}$, 1σ , $n=3$) (Saiz-Lopez et al. 2018). We evaluated the upper value of k_{red} (0.15 h^{-1}) for atmospheric aqueous Hg(II) photoreduction in the GEOS-Chem and GLEMOS Hg CTMs, and found that the observation-based, slow k_{red} leads to a major redox imbalance in the models. Model results showed a strong negative bias in the size of the Hg(0) pool and a positive bias in Hg(II) wet deposition (Saiz-Lopez et al., 2018). Based on theoretical chemistry computation of k_{red} , we proposed that gas phase photoreduction of Hg(II)BrX to Hg(I)Br is an alternative and fast reduction pathway for atmospheric Hg(II).

In this study we perform cation, anion and DOC analyses on the rainwater samples used by Saiz-Lopez et al. (2018), in order to assess the equilibrium speciation of atmospheric aqueous Hg(II). We present new experimental observations on the photoreduction rate constants of Hg bound to different types and concentrations of halides (Cl, Br, I ions) and to 1 mg.L^{-1} dissolved organic matter (DOM), in the form of fulvic acids. The objective of the present study is to better understand Hg speciation and dynamics in atmospheric waters, from an equilibrium speciation and photoreduction kinetics perspective. We aimed to identify in particular the nature of the slow reducing Hg(II) complexes in rainfall.

2. Materials and methods

2.1. Sampling and experimental preparation

Twenty-three experimental solutions containing Hg(II), DOM and halogen were prepared from commercially available NIST 3133 Hg, SRFA and halides (KCl, KBr, KI). The NIST SRM 3133 (10,000 $\mu\text{g g}^{-1}$ Hg(II) in 10 vol.% HNO₃) was used as Hg standard, from which more diluted stock solutions were prepared. Suwannee river fulvic acid (SRFA) was obtained from the International Humic Substances Society and dissolved in MQ water for use as a source of natural DOM (Maizel and Remucal 2017). KBr, KI and KCl salts were obtained from Sigma-Aldrich and diluted to 0.1 mM stock solutions. Collection of 12 rainfall events was previously detailed in Saiz-Lopez et al. (2018) (Saiz-Lopez et al. 2018). In brief, rainfall was collected at two different sites: in sub-urban Toulouse, France (n= 8, 1.479°E, 43.562°N) and at the high altitude (2877 m a.s.l.) Pic du Midi Observatory (PDM), France (n=2, 0.142°E, 42.937°N) in the summer of 2017 (Fu et al. 2016, Maruszczak et al. 2017). Large volume rain water was collected in 8 acid-cleaned polypropylene buckets simultaneously following Enrico et al. (2016) (Enrico et al. 2016). Single event samples were transferred to 2L acid-cleaned pyrex bottles with GL45 caps. Selected samples were filtered on pre-burnt 47mm quartz fiber filters (Millipore) in an acid-cleaned polycarbonate filtration unit (Fisher Scientific). Subsamples of filtered and unfiltered rainwater were taken for total Hg (THg, 10mL, acidified to 0.4 vol.% with bi-distilled 9N HCl, 0.5 vol% BrCl), TOC/DOC (20mL, acidified to 0.4 vol.% with 9N HCl), anions, pH (30mL, unacidified), and major and trace metals (10mL, acidified to 2 vol.% 15.8N HNO₃). Remaining rain samples were stored in the refrigerator in the dark at 4°C until analysis.

2.2. Photoreduction experiments

147 Photochemical experiments were carried out in a 60mm diameter, 0.5 L quartz reactor. For
148 controlled indoor laboratory experiments (Xenon lamp light) a Sutter Instruments Lambda LS
149 solar simulator with Perkin Elmer 300W PE300BUV Xenon lamp was used to shine artificial
150 solar light, corresponding to a solar light unit, (in the UVA, UVB, UVC, VIS and IR range) in a
151 40mm focused parallel beam through the reactor. Light intensities of key wavelengths of
152 artificial solar irradiation were measured with a solar light PMA 2200 radiometer, including
153 PMA 2106, PMA 2110 and PMA 2130 for UV-B (280-320nm), UVA(320-400nm) and visible
154 light (400-780nm) detector respectively (Supplementary Table S1). Outdoor experiments were
155 performed under natural sunlight (summertime, from 10-18h in full sun) outside the GET
156 laboratory building in Toulouse, France. No formal actinometric calibration of the experimental
157 set-up was performed. Instead we inter-compared Xe lamp experiments to outdoors full sunlight
158 experiments, which yielded similar Hg(II) reduction rates. Dynamic changes of natural UV and
159 visible irradiation intensities of these experiment days were simultaneously measured once per
160 hour and put in Supplementary Table S2. Rainfall experiments were done at both ambient Hg
161 levels, and at 2-40× augmented Hg levels. Experiments on artificial Hg-halogen solutions were
162 carried out at higher Hg concentrations (8-100 µg/L) with the goal to analyze Hg stable isotope
163 fractionation (data not shown here). Although, the NIST3133 Hg standard solution is prepared in
164 10 vol.% HNO₃, the amounts of NO₃⁻ introduced into the reactor are relative small, ~ 16 µM.
165 Since photoreaction of NO₃⁻ can generate a cascade of radical reactions, we compared NIST Hg
166 additions to natural rainwater samples, and found no significant difference in Hg(II) reduction
167 rate, suggesting absence of NO₃⁻ related bias. Experimental Hg/halide ratios were chosen to
168 approximate the range of natural ratios. Following sample addition, the reactor was wrapped
169 with aluminum foil and equilibrated overnight. At the start of photoreduction experiment a

sample aliquot ($t=0$) was taken and the reactor was exposed to natural sunlight outdoors (up to 8h) or to a solar simulator indoors (up to 48h). During the experiment the reactor was continuously purged with Hg-free argon gas at 80 mL min^{-1} to remove product $\text{Hg}(0)$ within minutes (O'Driscoll et al. 2006). Higher flow rates of 300 mL min^{-1} were tested and gave identical results, suggesting that the flow rate had no effect on observed the gross photoreduction rate. Subsamples were collected at different intervals over the course of the experiments. Dark control experiments were carried out under the same conditions in the absence of light irradiation. Analysis of the photoreduction product $\text{Hg}(0)$ was attempted, but failed due to leaks on the quartz reactor cap, which is a common problem in these type of experiments.

2.3. Hg, pH, cations and anions, DOC measurement

Samples were measured for total Hg concentration in duplicate following U.S. EPA method 1631 by cold vapor atomic fluorescence spectrometry (CV-AFS) in 5 ml aliquots at fixed time steps. CV-AFS analysis accuracy was evaluated by regular analysis of the NRC ORMS-5 certified reference material (26.2 ng/L) with good results (25.2 ± 3.3 , 1σ , $n=79$). The pH of all the rain samples and experimental solutions were measured as soon as possible after collection and preparation using an Orion pH electrode, calibrated against NIST traceable standards of pH 4 and 7. Major cations in rainfall and experimental solutions were analyzed by high resolution ICP-MS (Thermo-Scientific Element-XR) at OMP, Toulouse, France. Anions were analyzed by ion exchange chromatography at EcoLab, Toulouse, France. DOC or TOC was measured on a total organic carbon analyzer (Shimadzu TOC VSCN) at GET, Toulouse, France.

2.4. Gross photoreduction kinetics

The photoreduction experiments are considered as gross photoreduction due to the continuous purging of 80 mL min⁻¹ Hg-free argon gas in the reactor, which removes product Hg(0) and prevents it from re-oxidation to Hg(II). Dissolved Hg(II) is thought to be present as Hg(II)-ligand (Hg(II)L) complexes and reduced to Hg(0) in the presence of simulated solar light (Eq.1). The whole reduction process is considered as a pseudo first-order reduction reaction with rate constant, k_{red} (Eq.2) (Xiao et al. 1995, O'Driscoll et al. 2006, Qureshi et al. 2011).

$$\frac{d[\text{Hg(II)L}]}{dt} = -k_{\text{red}} \times [\text{Hg(II)L}], \quad (\text{Eq.2})$$

where Hg(II)L is the complexed inorganic Hg(II) in the solution, Hg(0) is the produced dissolved gaseous mercury (DGM) during the photoreduction process, $h\nu$ is the light irradiation including natural sunlight or xenon lamp light. In order to see whether our photoreduction reactions are pseudo first-order one, $\ln \frac{[\text{Hg(II)L}]_t}{[\text{Hg(II)L}]_0}$ is plotted as a function of time (h) shown in Supplementary Fig. S1a-e. Result show that generally the data show strong linear relationships (r^2 of 0.69-1) and the pseudo-first order approach is therefore appropriate.

2.5. Aqueous Hg speciation modeling

The speciation of dissolved Hg in rain water and experimental solutions was calculated using the geochemical equilibrium modeling software Visual Minteq version 3.1 with default parameters.

The input data were based on pH, temperature (22°C), Hg concentration, DOC concentration, cation types and concentrations (Rb, Mo, Cd, Ba, La, Tl, Pb, Th, U, Na, Mg, Al, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Sr and K), anion types and concentrations (F⁻, Cl⁻, N-NO₂⁻, Br⁻, N-NO₃⁻, S-

SO₄²⁻, P-PO₄³⁻). Trace metal, incl Hg(II), ion – DOC binding in Visual Minteq is based on the Stockholm Humic Acid Model with the shmgeneric14.vdb database (Gustafsson 2001), and which has been validated for Hg(II) elsewhere (Richard et al. 2016). Since atmospheric humic-like substances are generally low molecular weight compounds, and we use SRFA as a surrogate, we simulate equilibrium Hg(II) binding to fulvic acids only with binding constant logK_{HgFA2} of 6.7, and Lk2 spread factor of 3.2. At our experimental rainfall Hg/DOC ratios of 0.5 to 6.8 ng.mg⁻¹, Hg(II) is coordinated to thiol groups on the DOC compounds (Haitzer et al. 2002), which is represented in visual Minteq by the Hg(II)-FA2 complexes in the database and equilibrium speciation results. The nominal pH was 4 in all experimental solutions, and ranged from 3.8 to 6.3 in rainwater samples. No buffer was used to stabilize pH, in order to avoid photochemical artifacts, and in general drift in pH was limited to not more than 0.2 units.

3. Results and Discussion

3.1. Photoreduction of aqueous Hg(II)-halide, Hg(OH)₂ and Hg(II)-DOC

Experimental photoreduction of Hg(II) in the presence of different types of halides and different ratios of Br⁻/DOC were carried out to explore the influence of halide types and Br⁻/DOC ratios on Hg(II) photoreduction rates (Table 1). The photoreduction kinetics are shown in Fig. 1a-c indicate that different Hg(II) reduction rates occurred in all experiments including dark control and photo-induced conditions. Table 2 (exp. A3-A6) shows estimated equilibrium Hg(II) speciation at the start of the 0.1 mM halogen experiments, indicating that HgCl_{2(aq)} (97%), HgBr_{2(aq)} (98%) and HgI_{2(aq)} (62%) + HgI_{3⁻(aq)} (37%) were dominant. Two types of Hg(II) control experiments were carried out: exp. A1, presence of light, in MQ water, suggesting Hg(OH)_{2(aq)} as

the dominant species (95%), and exp. A2, A3, two dark controls (i.e. no light), in MQ with 95% $\text{Hg}(\text{OH})_{2(\text{aq})}$, and in presence of 0.2mM KBr with 95% $\text{HgBr}_{2(\text{aq})}$.

We observed low, but measurable, dark control reduction rates, k_{red} , of 0.009 h^{-1} for the $\text{Hg}(\text{OH})_{2(\text{aq})}$ complex in MQ water, and 0.001 h^{-1} for the $\text{HgBr}_{2(\text{aq})}$ complex (Fig. 1a, Table 1 experiments A2, A3). Dark reduction is generally attributed to abiotic, non-photochemical $\text{Hg}(\text{II})$ reduction and/or microbial $\text{Hg}(\text{II})$ reduction. Under full solar illumination by the Xe lamp, the stronger Hg-halide complexes resulted in progressively slower $\text{Hg}(\text{II})$ photoreduction rates, k_{red} , of 0.016 h^{-1} , 0.004 h^{-1} , for HgCl_2 , HgBr_2 , and undetectable for $\text{HgI}_2/\text{HgI}_3^-$ (Fig. 1b, Table 1 experiments A4, A5, A6). Experiments with F^- ion were attempted, but unsuccessful as F^- binds only weakly to $\text{Hg}(\text{II})$, resulting in dominant $\text{Hg}(\text{OH})_2$ complexes under all environmentally relevant F^- concentrations. The light control experiment in absence of halides resulted in a fast photoreduction rate of the $\text{Hg}(\text{OH})_{2(\text{aq})}$ complex in MQ water with k_{red} of 0.022 h^{-1} (Fig. 1a, Table 1 experiment A1). The fastest photoreduction was observed for Hg-DOC complexes with k_{red} of 0.23 h^{-1} (Fig. 1a, Table 1 experiment A7), which is slightly lower than published rate constants under similar conditions: $k_{\text{red}} = 0.47 \text{ h}^{-1}$ (Bergquist and Blum 2007), and a literature review on aqueous $\text{Hg}(\text{II})$ photoreduction in continental and marine waters with median $k_{\text{red}} = 0.41 \text{ h}^{-1}$ (Qureshi et al. 2011). Duplicate experiments on Hg-DOC and on HgBr_2 species resulted in typical uncertainties of 30% (1σ) on k_{red} . The dark control experiment with $\text{Hg}(\text{OH})_2$ (Fig. 1a, exp.A2) shows in fact a k_{red} that is faster (0.009 h^{-1}) than some of the Hg-halide photoreduction experiments, e.g. HgBr_2 at 0.004 h^{-1} . We suggest that the absence of stabilizing halide or DOC ligands in solution renders this dark control not representative of the true experimental or environmental dark $\text{Hg}(\text{II})$ reduction rates. The low dark control k_{red} of 0.001 h^{-1} of $\text{Hg}(\text{II})$ in the presence of Br is likely more representative (exp. A3).

Previous studies on Hg(II)-halide photochemistry suggested that ligand to metal charge transfer due to UVC absorption in the 200-300nm wavelength range can result in Hg(0) or Hg(I) products depending on Hg/halide ratio and presence of oxygen (Horvath and Vogler 1993). At our experimental conditions, under low UVC irradiation, and with molar Hg/halide ratios >100 and in absence of oxygen, Hg(0) should be the product. Xiao et al. (1994), performed similar experiments on Hg(OH)_{2(aq)} photoreduction at a higher pH of 7, finding k_{red} of 0.43 h⁻¹ which is 7x faster than our observations (Xiao et al. 1994). The difference is likely due to a different experimental set-up, possibly due to their use of a more powerful (450W) medium pressure Hg vapor lamp. Compared to a Xe lamp which reproduces a solar light spectrum, medium pressure Hg vapor lamps emit primarily in the 200-600nm region, with a particularly strong UVA line at 365.4 nm.

3.2. Photoreduction of Hg(II) in the presence of both halides and DOC

Photoreduction kinetics of Hg vary at different Br⁻/DOC ratios in the presence of halide and DOC (Fig. 1b). The pseudo first-order reduction rate constant k_{red} reached a high value of 0.23 h⁻¹ in the absence of Br⁻ (Table 1, exp.A7). Addition of Br⁻ at a low Br⁻/DOC ratio of 0.002mol.g⁻¹ resulted in a decreased k_{red} to 0.14h⁻¹, and approximately 98% of Hg(II) was reduced during 48h (Table 1, exp.A8). The continuous increase in Br⁻/DOC ratio further inhibits Hg photoreduction to reach 0.001h⁻¹ at a Br⁻/DOC ratio of 20mol.g⁻¹ and results in only about 7% of Hg(II) loss in the solution (Table 1, exp.A9-A12). Our experiments revealed that k_{red} had a strong linear correlation with the Br⁻/DOC ratios during 48h (Fig.2).

Composition calculation of the dominant Hg(II) species in the Br⁻ + DOC system are shown in Table 2 and show a progressive change from DOC dominated to Br⁻ dominated Hg(II)

coordination with the increase of Br/DOC from 0.002 mol.g⁻¹ to 20 mol.g⁻¹. When Br/DOC > 0.2 mol g⁻¹, HgBr_{2(aq)} is the dominant species (84%), whereas at Br/DOC < 0.2 mol g⁻¹, Hg-DOC dominates. These mixed ligand experiment show coherent behavior of Hg(II) photoreduction rates, varying between the fast (Hg-DOC) and slow (HgBr₂) end-members (Fig. 2). Additional experiments at Cl⁻/DOC of 0.2 mol g⁻¹, with calculated speciation of HgCl₂ (48%) and Hg-DOC (50%), resulted in a k_{red} of 0.16 h⁻¹. An I⁻/DOC = 0.2 mol g⁻¹ experiment resulted in a slow k_{red} of 0.0023 h⁻¹ during the first 72h, followed by insignificant Hg(II) photoreduction from 72 to 168h (Figure 1(c)). The decrease in k_{red} from 0.16 to 0.011 to 0.0023 h⁻¹ for the Cl⁻, Br⁻, I⁻ mixed ligand experiments in the presence of constant DOC concentration corroborates the role of the halide ion in stabilizing Hg(II) in solution (K_{eq} increasing from Cl⁻ to Br⁻ to I⁻), and effectively inhibiting photoreduction relative to Hg-DOC species. The inhibitory effect of halogen ligands on photoreduction can be explained by different photosensitizer properties of the halogens and DOC ligands. DOC contains chromophore moieties such as aromatic rings and conjugated double bonds which efficiently absorb UV-light at multiple wavelengths (Del Vecchio and Blough 2002). On the contrary, the ionic single bond of Hg(II)-X has more restricted UV absorption properties, likely leading to lower photoreduction yields (Saiz-Lopez et al. 2018).

3.3. Photoreduction of rainfall Hg(II)

We previously published experimental rainfall Hg(II) gross photoreduction rates, which ranged from 0.016 to 0.072 h⁻¹ (mean 0.051 ± 0.019 h⁻¹, σ , n = 10) in suburban Toulouse, and from 0.14 to 0.19 h⁻¹ (mean 0.15 ± 0.01 h⁻¹, σ , n = 3) at the remote high-altitude PDM (Saiz-Lopez et al. 2018). Here we complete this dataset with rainfall chemistry data for the same samples, including major cations, anions (including Cl⁻, Br⁻ and F⁻, but not I⁻), pH and DOC (Table 1,

experiments R1-R13). We use V. Minteq to estimate the Hg(II) species distribution among inorganic (F^- , Cl^- , Br^- , NO_3^- , SO_4^{2-} , OH^-) and organic, DOC ligands, assuming that equilibrium conditions are met, and that the rainfall is saturated in CO_2 with respect to an atmospheric pCO_2 of 400 ppmv. Particulate Hg(II) forms are ignored in the speciation calculations based on the low (<5%) particulate Hg detected by filtration. For I, we assume a total concentration of $1.1 \mu g L^{-1}$, identical to the mean rainfall total I observed at PDM (Suess et al. 2019). In the V. Minteq speciation model we assumed atmospheric DOC to be in the form of strong fulvic-type acids (FA2). Speciation calculation results are summarized in Table 2, and indicate that in all rainfall samples Hg is bound to DOC, notably to the stronger FA2 type sites that represent phenolic, thiol and bidentate complexes with Hg(II). The Hg/DOC concentration ratios we observe in rainfall range from 0.5 to $6.8 ng.mg^{-1}$, indicating that Hg(II) is likely coordinated to thiol groups on the DOC compounds (Haitzer et al. 2002). Observed Cl^-/DOC , Br^-/DOC and estimated I^-/DOC levels in rainfall range from 0.02 to $6 \times 10^{-7} mol/g$, corroborating that the photoreduction kinetics should be dominated by the Hg(II)-DOC experimental end-member.

Fig. 3. shows a negative relationship between rainfall DOC and Hg(II) photoreduction rate (k_{red} , h^{-1} ; $r^2 = 0.91$). The relationship is driven by the PDM data which has lower DOC and faster k_{red} . Within the urban rainfall data, the DOC vs k_{red} relationship remains significant, but less pronounced ($r^2 = 0.24$) (Supplementary Fig. S2). The variation in rainfall k_{red} is not driven by Hg/DOC ratio ($r^2 = 0.14$) (Supplementary Fig. S3). We observed no statistically significant ($p > 0.05$) differences between rainfall Hg(II) reduction rates under natural ($0.063 \pm 0.026 h^{-1}$, 2σ , $n=3$) and simulated sunlight ($0.037 \pm 0.032 h^{-1}$, 2σ , $n=5$). We suggest that the overall DOC vs. k_{red} trend in Fig. 3 is possibly driven by rainfall DOM molecular properties, likely to be different in the urban boundary layer and free troposphere. One possible reason may be the partial

oxidation of thiol groups in atmospheric DOC at the remote PDM site (Tyndall and Ravishankara 1991). A lower availability of the high-affinity thiol ligands should result in weaker complexation of Hg(II) by low affinity O/N ligands and therefore faster photoreduction rates (Jiang et al. 2015). A more detailed characterization of DOC is needed to understand this observation. Fig. 4. summarizes published k_{red} and our experimental and rainfall k_{red} observations. Rainfall k_{red} are of similar magnitude as the lower (slower) end of k_{red} in terrestrial and marine waters. Once more this points to differences in OM, Hg-OM properties and trace metal : OM ratios in atmospheric, terrestrial and marine waters. Understanding the influence of aquatic geochemistry on Hg photoreduction rates requires investigating all three water types with the same experimental and analytical techniques.

4. Conclusions

In this study we performed Hg(II) photoreduction experiments in the presence of halides (Cl, Br, I) and DOC. The Hg(II) photoreduction rates observed in rainwater (0.05 h^{-1} in urban to 0.15 h^{-1} in remote rainfall) are faster than those of isolated HgBr_2 complexes (0.004 h^{-1}), and resemble more the rates of Hg(II)-DOC compounds (0.23 h^{-1}). Our observations on experimental and rainfall Hg(II) photoreduction rates and on estimated Hg(II) speciation in rainfall lead to a number of suggestions on cloud water Hg chemistry. Previous research on gas-phase Hg chemistry has shown that elemental Hg emissions are partially oxidized by a two-step mechanism, involving Br radicals in step 1, and NO_2 , HO_2 radicals in step 2, to produce Hg-halide end products HgBr_2 , HgBrOH , HgBrONO , HgBrOHO (Horowitz et al. 2017, Saiz-Lopez et al. 2018). These gaseous oxidized Hg(II) compounds are water soluble and therefore partition efficiently into aqueous aerosols and eventually in cloud water and rain (Amos et al. 2012,

350 Horowitz et al. 2017). Aerosols contain abundant organic carbon, in large excess over halide ions,
351 which is reflected in the low halide/DOC ratios of rainfall observations ($0.04 - 0.75 \text{ g g}^{-1}$).
352 Despite the strong binding properties of halide ions towards Hg(II), our equilibrium Hg(II)
353 speciation calculations, and experimental photoreduction rate observations suggest that
354 scavenged Hg-halide complexes are rapidly transformed into aqueous Hg-DOC complexes in
355 rainfall, and by extension in cloud-water.

356

357

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367

368 **Figures and tables**

370 Figure 1a-c. Experimental photoreduction rates of 100ppb (0.5um) dissolved Hg(II) were carried
 371 out: a) in the presence of different types of halides (experiment nos. A4-A6, table 1) and for light
 372 and dark control experiments (experiments nos. A1-A3, table 1), b) in the presence of different
 373 Br⁻/DOC ratios (experiment nos. A7-A12, table 1), c) in the presence of different types of
 374 halide/DOC (experiment nos. A13 and A14, table 1). SRFA, Suwannee river fulvic acid.

375

376

377 Figure 2. Hg(II) photoreduction rates are plotted against different Br⁻/DOC ratios (experiments
 378 A7-A11, Table 1).

379
 380 Figure 3. Rainfall DOC (mg.L⁻¹) plotted as a function of rainfall Hg(II) photoreduction rate (h⁻¹)
 381 in the presence of xenon lamp light and natural sunlight. The regression line includes all data.
 382
 383

Figure. 4. Comparison of experimental and model photoreduction rates of Hg(II) in different media. In-cloud model maximum k_{red} were approximated from the rate constant expressions in Selin et al., 2007 (assuming typical, maximum $[\text{OH}]$ of $10^6 \text{ molecules cm}^{-3}$), and Horowitz et al., 2017 (assuming typical values of j_{NO_2} of 10^{-2} s^{-1} and maximum organic aerosol levels, $[\text{OA}]$ of $1 \mu\text{g m}^{-3}$), and amount to 1 h^{-1} , and 2.3 h^{-1} respectively.

Table 1. Compositions and conditions of experimental Hg and rainfall solutions of photoreduction experiments. A and R represent experimental Hg solution and rainfall solution. UF and F indicate unfiltered and filtered rainfall. Xe represents xenon solar simulator. TL and PDM indicate sub-urban Toulouse sample and high altitude (2877 m a.s.l.) Pic du Midi Observatory samples. SRFA, Suwannee river fulvic acid; HgFA2 indicates Hg-fulvic acid complex at strong type 2 sites in Visual Minteq.

Exp no.	Figure legend	dominant Hg species	k_{red} h ⁻¹	pH	Light	Hg ng.mL ⁻¹	DOC mg.L ⁻¹	Hg/DO C ng.mg ⁻¹	halide	halide A mM	SRF mg.L ⁻¹	Hg/halide mg.mol ⁻¹	halide/DO C mol.g ⁻¹
A1	Hg-Xe light	Hg(OH) ₂	0.022	4.1	Xe	100	/	/	/	/	/	/	/
A2	Hg-dark control	Hg(OH) ₂	0.009	4.1	Dark	100	/	/	/	/	/	/	/
A3	Hg-0.2mM KBr-dark control	Hg(Br) ₂	0.001	4.1	Dark	100	/	/	KBr	0.2	/	500	/
A4	Hg-0.1mM KCl-Xe light	Hg(Cl) ₂	0.16	4.2	Xe	100	/	/	KCl	0.1	/	1000	/
A5	Hg-0.2mM KBr-Xe light	Hg(Br) ₂	0.004	4.2	Xe	100	/	/	KBr	0.2	/	500	/
A6	Hg-0.1mM KI-Xe light	Hg(I) ₂	n.a.	4.0	Xe	100	/	/	KI	0.1	/	1000	/
A7	Hg-1mg/L SRFA-Xe light	HgFA2	0.23	7	Xe	100	0.5	200000	/	/	1	/	/
A8	Hg-0.001mM KBr-1mg/L SRFA-Xe light	HgFA2	0.14	4.1	Xe	100	0.5	200000	KBr	0.001	1	100000	0.002
A9	Hg-0.01mM KBr-1mg/L SRFA-Xe light	Hg(Br) ₂	0.046	4.1	Xe	100	0.5	200000	KBr	0.01	1	10000	0.02
A10	Hg-0.1mM KBr-1mg/L SRFA-Xe light	Hg(Br) ₂	0.011	4.1	Xe	100	0.5	200000	KBr	0.1	1	1000	0.2
A11	Hg-1mM KBr-1mg/L SRFA-Xe light	Hg(Br) ₂	0.006	4.1	Xe	100	0.5	200000	KBr	1	1	100	2
A12	Hg-10mM KBr-1mg/L SRFA-Xe light	Hg(Br) ₂	0.001	4.1	Xe	100	0.5	200000	KBr	10	1	10	20
A13	Hg-0.1mM KCl-1mg/L SRFA-Xe light	HgFA2	0.16	4.2	Xe	100	0.5	200000	KCl	0.1	1	1000	0.2
A14	Hg-0.1mM KI-1mg/L SRFA-Xe light	Hg(I) ₂	0.002	7	Xe	100	0.5	200000	KI	0.1	1	1000	0.2
						ng.L ⁻¹			F ⁻ mg.L ⁻¹	Cl ⁻ mg.L ⁻¹	Br ⁻ mg.L ⁻¹	I ⁻ mg.L ⁻¹	
R1	Rain event 1-U-Xe light-TL	HgFA2	0.043	4.7	Xe	9.0	2.14	4.2	0.02	0.88	0.002	0.0011	14.8
R2	Rain event 1-U-Xe light-TL	HgFA2	0.071	4.4	Xe	82	2.14	38	0.02	0.88	0.002	0.0011	14.8
R3	Rain event 2-F-Xe light-TL	HgFA2	0.064	4.1	Xe	89	2.10	42	0.02	0.26	0.002	0.0011	4.5
R4	Rain event 3-U-Xe light-TL	HgFA2	0.016	6.3	Xe	89	3.47	26	0.02	0.19	0.003	0.0011	2.0
R5	Rain event 4-F-Natural light-TL	HgFA2	0.069	6.1	Sun	88	1.42	62	0.01	0.091	0.001	0.0011	2.3
R6	Rain event 5-F-Natural light-TL	HgFA2	0.047	6.3	Sun	91	0.84	108	0.01	0.63	0.002	0.0011	27.0
R7	Rain event 5-F-Dark control-TL	HgFA2	0.007	6.3	dark	92	0.84	110	0.01	0.63	0.002	0.0011	27.0
R8	Rain event 8-U-Natural light-TL	HgFA2	0.071	5.1	sun	2.6	2.46	1.0	0.01	0.1	0.001	0.0011	1.5
R9	Rain event 8-U-Xe light-TL	HgFA2	0.047	5.1	Xe	2.5	2.46	1.0	0.01	0.1	0.001	0.0011	1.5
R10	Rain event 8-U-Xe light-TL	HgFA2	0.031	3.8	Xe	103	2.46	42	0.01	0.1	0.001	0.0011	1.5
R11	Rain event 9-U-Xe light-PDM	HgFA2	0.15	5.9	Xe	2.3	0.75	3.0	0.01	0.039	n.a.	0.0011	1.9
R12	Rain event 10-U-Xe light-PDM	HgFA2	0.19	6.1	Xe	2.0	0.28	7.1	0.01	0.031	n.a.	0.0011	4.0
R13	Rain event 10-U-Xe light-PDM	HgFA2	0.14	6.1	Xe	2.0	0.28	7.1	0.01	0.031	n.a.	0.0011	4.0

409 Table 2. Equilibrium Hg(II) speciation of 100ppb (0.5 μ M) experimental Hg solutions and
 410 rainfall solutions. /FA2Hg indicates Hg(II) bound to the strong (type 2) fulvic acid (FA) sites in
 411 the Stockholm Humic Acid model that simulates equilibrium Hg – humic interaction in the
 412 Visual Minteq software.

Experiment no. Experiment name		Hg(II) species and percentage				
		species (%)	species (%)	species (%)	species (%)	species (%)
A1/A2	Hg+Xe light/dark control	Hg ²⁺ 0.96	HgOH ⁺ 4	Hg(OH) ₂ 95		
A3/A5	Hg+ 0.2mM KBr+dark control/Xe light	HgBr ₂ (aq) 95	HgBr ₃ ⁻ 5	HgBr ₄ ²⁻ 0.02	HgBrOH (aq) 0.01	
A4	Hg+ 0.1mM KCl+Xe light	HgCl ⁺ 0.21	HgCl ₂ (aq) 97	HgCl ₃ ⁻ 0.10	HgClOH (aq) 3	Hg(OH) ₂ 0.02
A6	Hg+ 0.1mM KI+Xe light	HgI ₂ (aq) 62	HgI ₃ ⁻ 37	HgI ₄ ²⁻ 0.33		
A7	Hg+ 1mg/L SRFA	Hg ²⁺ 0.03	/FA2Hg (aq) 97	HgOH ⁺ 0.13	Hg(OH) ₂ 2.634	
A8	Hg+ 0.001mM KBr + 1mg.L ⁻¹ SRFA+Xe light	HgBr ⁺ 0.28	HgBr ₂ (aq) 46	/FA2Hg (aq) 52	HgBrOH 1.45	Hg(OH) ₂ 0.014
A9	Hg+ 0.01mM KBr + 1mg.L ⁻¹ SRFA+Xe light	HgBr ⁺ 0.02	HgBr ₂ (aq) 70	HgBr ₃ ⁻ 0.16	/FA2Hg (aq) 30	HgBrOH 0.13
A10	Hg+ 0.1mM KBr + 1mg.L ⁻¹ SRFA+Xe light	HgBr ₂ (aq) 90	HgBr ₃ ⁻ 2	HgBrOH 0.02	/FA2Hg (aq) 7	
A11	Hg+ 1mM KBr + 1mg/L SRFA+Xe light	HgBr ₂ (aq) 77	HgBr ₃ ⁻ 18	HgBr ₄ ²⁻ 0.34	/FA2Hg (aq) 5	
A12	Hg+ 10mM KBr + 1mg/L SRFA+Xe light	HgBr ₂ (aq) 25	HgBr ₃ ⁻ 60	HgBr ₄ ²⁻ 13	/FA2Hg (aq) 2	
A13	Hg+ 0.1mM KCl + 1mg/L SRFA	HgCl ⁺ 0.10	HgCl ₂ (aq) 48	HgCl ₃ ⁻ 0.05	/FA2Hg (aq) 50	HgClOH (aq) 1.42
A14	Hg+ 0.1mM KI + 1mg/L SRFA	HgI ₂ (aq) 62	HgI ₃ ⁻ 37	HgI ₄ ²⁻ 0.33	/FA2Hg (aq) 0.08	
		Species (%)	percentage (%)			
R1	Rain event 1-U-Xe light-TL	/FA2Hg (aq)	100			
R2	Rain event 1-U-Xe light-TL	/FA2Hg (aq)	100			
R3	Rain event 2-F-Xe light-TL	/FA2Hg (aq)	100			

R4	Rain event 3-U-Xe light-TL	/FA2Hg (aq)	100
R5	Rain event 4-F-Natural light-TL	/FA2Hg (aq)	100
R6	Rain event 5-F-Natural light-TL	/FA2Hg (aq)	100
R7	Rain event 5-F-Dark control-TL	/FA2Hg (aq)	100
R8	Rain event 8-U-Natural light-TL	/FA2Hg (aq)	100
R9	Rain event 8-U-Xe light-TL	/FA2Hg (aq)	100
R10	Rain event 8-U-Xe light-TL	/FA2Hg (aq)	100
R11	Rain event 9-U-Xe light-PDM	/FA2Hg (aq)	100
R12	Rain event 10-U-Xe light-PDM	/FA2Hg (aq)	100
R13	Rain event 10-U-Xe light-PDM	/FA2Hg (aq)	100

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