Chapter 14
Our Current Understanding of Major Chemical and Physical Processes Affecting Mercury Dynamics in the Atmosphere and At the Air-Water/Terrestrial Interfaces

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Summary The predictions of atmospheric chemical models are limited by the accuracy of our understanding of the basic physical and chemical processes that underlie the models. In this work we review the current state of our knowledge of the chemical processes that transform atmospheric mercury species via gas and aqueous phase reactions and the physical processes of deposition. We concur with the conclusions of other recent reviews that our understanding of the basic chemistry that controls mercury is incomplete and the experimental data either limited or non-existent. In spite of this recent experimental and theoretical studies of mercury reaction kinetics have clarified some issues. Observations in Polar Regions suggest that Hg^0 can undergo fast oxidation in the presence of elevated levels of bromine compounds. Both experimental and theoretical studies suggest that the recombination of Hg^0 with Br atoms is sufficiently fast to initiate this oxidation process. However there is a large uncertainty in the value of the rate coefficient for this recombination reaction and in the fate of the reaction product, HgBr. Most global mercury models incorporate reactions of Hg^0 with OH and O_3. Based on the most recent high level ab-initio calculations of the stability of HgO it appears that neither of these reactions is likely to play a significant role in mercury oxidation. The most important aqueous oxidation for Hg^0 appears to be reaction with O_3 however that there has only been one determination of the $Hg + O_3$ reaction rate constant in the aqueous phase. Aqueous phase reduction of oxidized mercury via reaction with HO_2 is the only significant reduction reaction in current models but now seems unlikely to be significant. Again this suggests that the chemistry controlling mercury transformation in current models requires significant modification.

14.1 Introduction

Over the past decade our understanding of the chemical cycling of mercury has been changed, particularly by the recognition that homogeneous gas phase chemistry may play a significantly more important role in this cycling than was previously recognized.

In this chapter we have attempted to review the current state of mercury science with regard to the important chemical and physical processes that affect the atmospheric transformation of mercury and its rate of deposition. If we view the progress that has been made in our overall understanding of chemical cycling in the troposphere and stratosphere we see iterative interactions between three branches of atmospheric chemistry. The three branches are typically compartmentalized between modeling, field measurements and laboratory measurements. Laboratory measurements include both experimental and theoretical studies of the elementary processes that are important in atmospheric transformation and include both measurements and calculations of reaction rate coefficients, thermodynamics and spectroscopic properties of atmospheric species. These processes form the basic input to atmospheric models that are then used to predict the spatial and temporal distributions of atmospheric species. The output from models is then compared with field measurements and gives a measure of our detailed understanding of the processes that are taking place. We consider separately homogeneous gas phase transformation, liquid phase transformation and atmospheric deposition processes.

14.2   Homogeneous Gas Phase Transformation

Our understanding of the importance of gas phase chemistry in the biogeochemical cycling of mercury has gone through a complete transformation over the past decade. This has been driven by atmospheric observations and we briefly review these in the context of our overall understanding of tropospheric chemical cycling.

14.2.1   Field Observations

The seminal observation that led to a reassessment of mercury chemistry was provided by Schroeder and coworkers during a study of polar ozone depletion events (Schroeder et al., 1998). Observations of springtime ozone depletion have been known for over two decades and are linked to halogen chemistry, with bromine containing radicals thought to be the most important species. In 1998 Schroeder et al. reported the results of 1995 field observations at Alert, Canada that showed that for three months following polar sunrise there were frequent episodic depletions of gaseous elemental mercury which correlated strongly with depletions of ozone. Subsequently Lindberg et al. (2002) published a series of observations from Barrow, Alaska demonstrating the same phenomenon. They also incorporated measurements of RGM using a newly developed denuder technique. Again they observed a strong correlation between mercury and ozone depletion events and found that the depletion events were correlated with high column densities of BrO as measured by the GOME satellite. They also found that that RGM showed a strong diurnal profile indicating photochemical production of the species responsible

for Hg^0 oxidation. They proposed an oxidation mechanism based on Hg^0 reaction with bromine and chlorine atoms and the halogen monoxides. Subsequently these AMDEs (Atmospheric Mercury Depletion Events) have been observed by several groups in the springtime in both the Arctic and Antarctic.

Recently Peleg et al. (2007) reported the observation of diurnal cycles of mercury, ozone, and BrO behavior based on short-time resolution measurements near the Dead Sea, Israel, in Summer 2006. The results showed that mercury depletion events occurred almost daily, accompanied always by the presence of BrO and concurrent ozone destruction. The intensity of the MDE corresponded to increasing BrO levels. Mercury depletions of more than 40% were observed when BrO levels rose above 60 - 70 ppt.

In addition to mercury transformation that is clearly consistent with a halogen mediated oxidation mechanism a number of observations have suggested that elevated levels of RGM are present in the upper troposphere. Landis et al. (2005) monitored both Hg^0 and RGM in a series of flights in southern Florida in June 2000. During the flights, they monitored Hg^0 and RGM between 0.06 and 3.5 km and observed a small negative trend with altitude in Hg^0 and a more pronounced positive trend between RGM and increasing altitude. They observed RGM concentrations of 100 pg m^{-3} at the highest altitudes. The Landis et al. data set is the only aircraft data that has monitored both Hg^0 and RGM. Murphy and coworkers have obtained and analyzed the mass spectra of individual particles using a Particle Analysis by Laser Mass Spectroscopy (PALMS) instrument (Murphy et al., 2006a, 2006b). The extensive PALMS data set revealed that at the tropopause a large fraction of the observed particles in both the tropics and mid-latitudes contain Hg. In addition a single sample was collected in the lower stratosphere for analysis by Scanning Transmission Electron Microscopy. The distribution of Hg onto up to 70% of sampled particles, even small (20nm) particles is indicative of a local Hg(p) source rather than transport of Hg-rich aerosols from surface sites. The peak in aerosols containing Hg is centered at the tropopause with almost none of the particles sampled below 5 km containing Hg. This rapid decline could be due the re-volatilization of Hg or RGM from the aerosol once in the warmer troposphere or the rapid washout of Hg(p) and RGM during precipitation events. As the PALMS instrument measures both positive and negative ions it is of interest that Hg ions and Br^{-} follow a similar profile, indicating that they are present in the same aerosol species even if they are not chemical bound to each other.

A limited number of observations at elevated sampling sites at Mona Loa, Hawaii (Landis et al., 2005), and Mount Batchelor, Oregon (Swartzendruber et al., 2006) also show evidence for elevated RGM in the free and upper troposphere. Swartzendruber et al. (2006) saw elevated levels of RGM of up to 500 pg m^{-3} in subsiding air at Mount Batchelor. These air masses contained decreased levels of elemental gaseous mercury suggesting that total mercury was conserved and the RGM was a result of local conversion of Hg^0 to RGM in the upper troposphere.

These observations are clearly indicative of relatively rapid transformation of Hg^0 to RGM and suggest that gas phase chemistry is responsible. The observations of mercury depletion in polar regions and the Dead Sea are accompanied by

ozone depletion and elevated levels of bromine radicals and are clearly suggestive of halogen chemistry. Transformation in the upper troposphere carries no "chemical signature" which is suggestive of the chemical mechanism and oxidation via reaction with ozone, OH and Br atoms have all been considered as possible mechanisms. We now consider the potential oxidation chemistry that might be responsible for this transformation.

14.2.2   Kinetic of Homogeneous Gas Phase Reactions

In spite of the clear evidence for rapid, homogeneous gas chemistry involving reaction of gas phase elemental mercury with other atmospheric reactants, the identification of the specific chemistry remains elusive. As we review the limited amount of experimental and theoretical data available we try and apply two criteria 1) are the observations consistent with our understanding of basic physical chemistry and 2) are they consistent with field observations. As we discuss below recent calculations on the stability of diatomic gas phase HgO suggest that homogeneous gas phase oxidation of Hg^0 by O_3 is not a viable atmospheric oxidation pathway for Hg^0. Both calculations and observations suggest that weakly bound complexes of mercury may play a significant role, at least in laboratory experiments. Since an understanding of the kinetics, particularly of weakly bound complexes, can be difficult and may not be treated clearly in the mercury literature, we provide some background on basic kinetics, thermochemistry and atmospheric chemistry.

14.2.2.1   Terminology

We briefly review some of the basic terminology associated with this chemistry giving examples from tropospheric chemistry and some mercury specific examples. The bimolecular rate coefficient for the reaction of two species A and B to give products C and D:

$$A + B \rightarrow C + D$$
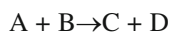
   is defined as

$$-d[A]/dt = -d[B]/dt = d[C]/dt = d[D]/dt = k[A][B]$$

where k is the rate coefficient. The rate coefficient is sometimes referred to as a "rate constant" but k will typically vary as a function of temperature and sometimes as pressure and hence rate coefficient is a preferred term. For the simplest type of bimolecular chemical reaction involving an abstraction reaction, k is typically independent of pressure and has a positive activation energy, E_a, as defined by the Arrhenius equation.

$$k\,(T) = A\,\exp\,(-\,E_a/RT)$$

where A is the pre-exponential factor.

The major oxidant in the troposphere is the hydroxyl radical and one of its major sinks is reaction with atmospheric methane. This is a simple H atom abstraction reaction to form water and methyl radicals.

$$CH_4 + OH \rightarrow CH_3 - H_2O \quad \Delta H^0 = -57.8 \text{ kJ} \cdot \text{mol}^{-1}$$

The rate coefficient is well described by an Arrhenius expression 1.85×10^{-12} $\exp(-1690/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200-300 K, which gives a room temperature rate coefficient of $k = 6.4 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K (Sander et al., 2006, Atkinson et al., 2006). Because this is a simple abstraction reaction this rate coefficient shows no dependence on pressure or bath gas composition. If this rate coefficient is measured at one atmosphere in air, or one Torr in He, by either relative or absolute methods, the same result should be obtained.

The rate coefficient can exhibit more complicated pressure and temperature dependencies for unimolecular and termolecular reactions and particularly complex behavior if reaction proceeds via formation of a weakly bound addition complex. Since it appears likely that HgO may form this type of a complex we describe an example of such a reaction and the type of behavior observed. Both carbon disulfide and the alkyl sulfides react with OH via the formation of weakly bound addition complexes that undergo further reaction with molecular oxygen (Hynes et al., 1988, Williams et. al., 2007). In the case of the alkyl sulfides this addition process proceeds in parallel with an abstraction channel, but for CS$_2$ reaction proceeds only via addition so this case will be identical to behavior we might expect from Hg^0. The reaction of CS$_2$ with OH is described by the following sequence of reactions (Hynes et al., 1988).

$$OH + CS_2 + M \leftrightarrow OHCS + M \qquad (2, \text{-}2)$$

$$OHCS_2 + O_2 \rightarrow products \qquad (3)$$
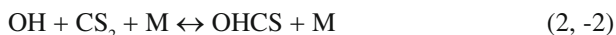
In such a system the results of an experimental investigation of the rate coefficient at any particular temperature will produce results that depend on the pressure, bath gas composition *and the temporal resolution of the experiment* !! If we attempt to measure the rate coefficient for this reaction in the absence of O$_2$ in an experiment with sub-microsecond time resolution or via a relative rate technique we will see no evidence for chemical reaction. If we measure using a direct technique with fast temporal resolution we can directly observe the equilibration (2,-2) (Hynes et al., 1988) and by analyzing the observed biexponential decays we can measure the rate coefficients for reactions 2 and -2 and hence the equilibrium constant. By measuring the equilibrium constant as a function of temperature we can the obtain the bond energy of the adduct. If we perform the same experiments in the presence of O$_2$ under conditions in which the concentration of the adduct is much smaller than that of OH we will observe a net loss of OH. If reaction is performed with the concentration of CS$_2$ in

large excess with respect to OH then we will see pseudo-first order decays of OH and we can define an "effective rate coefficient", k_{obs} which is given by:

$$k_{obs} = \frac{(k_3 / k_2) * k_2 * [O_2]}{1 + (k_3 / k_{-2}) * [O_2]}$$

The key point here is that k_{obs} is not a true elementary rate coefficient but rather a composite which is a function of the three elementary rate coefficients, the total pressure and the specific O_2 concentration. Since the three elementary rate coefficients show very different temperature dependencies the overall temperature dependence is complex, but, at least for CS_2 and the alkyl sulfides, is dominated by k_{-2}. As the temperature decreases k_{-2} decreases rapidly, hence for any particular conditions of total pressure and O_2 concentration, the effective rate coefficient increases rapidly as the temperature decreases! As we noted above, if we perform experiments at 298 K we will obtain a different value of k_{obs} each time we change the pressure or O_2 concentration. However if we are working under conditions in which the OH radical concentration is much greater than that of the adduct, conditions which apply in the real atmosphere, we will obtain the same value of k_{obs}, irrespective of how we actually perform the measurement, i.e. direct and relative rate techniques will give exactly the same result. This, of course, assumes that there are no artifacts due to secondary chemistry or other systematic errors.

14.2.2.2   Thermodynamics

The overall rate of a reaction is governed by an interaction between kinetics, a rate process, and thermodynamics, which considers the energetics of a process. Processes that are exothermic and increase the entropy of the system favor reaction. The balance between enthalpy, ΔH, and entropy, ΔS, is given by the Gibbs Free Energy.

$$\Delta G = \Delta H - T\Delta S$$

If Gibbs Free Energy is negative a reaction will proceed spontaneously from a thermodynamic perspective and we can calculate the equilibrium constant, K_p from:

$$\ln (K_p) = - \Delta G^0 / RT$$

and the ratio of the forward and reverse rate coefficients from:

$$K_c = k_f / k_r$$

In many cases a reaction that is thermodynamically favorable will not proceed at a measurable rate because a large endothermic barrier to reaction exists. In attempting to evaluate the available kinetic data on mercury chemistry it is useful to place this in the context of kinetic data evaluation. Typical models of atmospheric chemistry contain hundreds of chemical reactions and for the most critical reactions there will

be many independent determinations of the rate coefficients by multiple experimental techniques. Even though these experiments may have been published in the peer reviewed literature the rate coefficients that have been obtained can differ significantly and, as a consequence, two independent review panels were established to evaluate the published literature and recommend the value of the rate coefficient that would be appropriate for use in models together with an estimate of the uncertainty associated with the recommendation (Sander et al. 2006, Atkinson et al. 2006). In this context, for the most important reactions the range of uncertainty is less than a factor of two, based on multiple independent determinations by a variety of different experimental techniques. In contrast there are very few independent determinations of any reactions of Hg^0 and in most cases very large discrepancies exist in the published data. At the moment neither of the two international data panels includes mercury chemistry in their evaluations.

14.2.2.3   Experimental Approaches

Experimental approaches to the study of mercury kinetics can be broadly divided between absolute and relative rate methods. In direct measurements the rate of loss one reactant is monitored in the presence of a large excess of a second reactant. For very slow reactions, such as the reaction of mercury with ozone, chemistry can be initiated by physical mixing. For fast reactions, photolysis, using a laser or flash lamp is used. In relative rate methods the loss of mercury is measured relative to that of a reference compound. The rate coefficient for the reaction of the reference compound with the reactant of interest should be well known.

14.2.2.4   Ab-Initio Thermochemistry

The challenges with using ab-initio quantum mechanics to calculate the thermochemistry of mercury compounds has been discussed by Ariya and Peterson (2005). They note, in particular, the challenge in dealing with relativistic effects for a large element like mercury with eighty electrons, a result of the large nuclear charge. The ability of such calculations to calculate thermodynamic properties with "chemical accuracy" normally implies an uncertainty of ± 1 kcal mol^{-1}, the accuracy required to calculate rate coefficients within a factor of two or three of the actual rate. At this point it appears that Peterson and coworkers have been able to achieve something that certainly approaches "chemical accuracy" and, as we discuss below, this has profound implications for our evaluation of potential mercury oxidation reactions.

14.3   Specific Reaction Systems

Ariya and Peterson (2005) reviewed the kinetic data on mercury reactions and discussed some of the problems associated with measurements. In this review we have focused on a limited number of reactions that are currently used in models of mercury

oxidation or which may be of importance. In each case we detail our best estimate of the thermo-chemistry if such an estimate is feasible.

14.3.1 $Hg^0 + O_3$

$$Hg^0 + O_3 \rightarrow HgO + O_2 \qquad\qquad \Delta H = 93 \text{ kJ mol}^{-1} \qquad\qquad (4a)$$

$$Hg^0 + O_3 + M \rightarrow HgO_3 + M \qquad\qquad\qquad\qquad (4b)$$

There have been three recently published studies of this reaction. Hall (1995) studied the reaction of Hg^0 with O_3 as a function of temperature in a static configuration in Teflon reactors. He also investigated the effects of changes in the surface to volume (s/v) ratio and the effects of sunlight. Experiments were performed at atmospheric pressure in a gas mixture that was composed of N_2, with 2-10 % O_2, and with trace levels of Hg^0 and O_3 (20-1500 ppm). The decrease of Hg^0 and the formation of $Hg^{(II)}$ on the walls were monitored. Monitoring Hg^0 loss in an excess of O_3, i.e. under essentially pseudo first order conditions, the Hg^0 decays showed good pseudo first order behavior. Essentially quantitative conversion of Hg^0 to $Hg^{(II)}$ was observed and calculated rate coefficients were based on an assumed mechanism that included gas phase and wall reaction. Based on the change in rate coefficient observed when the s/v was changed Hall concluded that reaction was occurring in both the gas phase and on the reactor walls and a gas phase rate coefficient of $3 \pm 2 \times 10^{-20}$ cm^3 molecule^{-1} s^{-1} was derived. However the pseudo-first order rates did not depend linearly on $[O_3]$ and gave a reaction order of 0.8 with respect to O_3. Experiments were performed at two elevated temperatures and the rate coefficient was found to increase with temperature. Expressing the data in Arrhenius form gave an A factor of 2.1×10^{-18} cm^3 molecule^{-1} s^{-1} and an activation energy of 10 kJ mol^{-1}, however the large uncertainty in the value of the heterogeneous component of the rate produces a very large uncertainty in these values which is not discussed in the paper. The rate coefficient showed no dependence on relative humidity but it was found to increase in the presence of sunlight, a result that might be due to either gas phase or surface reactions. No in-situ diagnostics were employed to confirm that reaction products were being formed in the gas phase.

Pal and Ariya (2004) used both relative and absolute measurement approaches to study this reaction. They noted that the kinetics appeared to be very sensitive to the nature of the wall and coated their reaction vessels with halocarbon wax to minimize surface chemistry. The relative rate studies monitored the decay of Hg^0 relative to that of propone or 1-butene in an excess of N_2 buffer gas at 750 Torr total pressure. They reported five rate coefficients between 15 and 7×10^{-19} cm^3 molecule^{-1} s^{-1} and concluded that the reactions of the reference molecules with O_3 produced OH radicals that initiated secondary chemistry. In two experiments trimethylbenzene was added to reaction mixtures to scavenge the OH radicals giving rate coefficients of 7×10^{-19} cm^3 molecule^{-1} s^{-1}. In the absolute measurements Hg^0 decays were monitored

in an excess of O_3 at several surface to volume ratios. The decays showed a complex behavior and the authors attributed the initial component of the decays to a simple gas phase reaction, the second component to a surface enhanced reaction and they obtained a rate coefficient of $(7.5\pm0.9) \times 10^{-19}$ cm^3 molecule^{-1} s^{-1}. No in-situ diagnostics were employed to confirm that reaction products were being formed in the gas phase. Analysis of volatile surface reactants, using chemical ionization mass spectroscopy, produced evidence for a HgO containing species. As we discuss below Tossell (2003) has reported calculations that suggest that oligomers of HgO are much more strongly bound than the diatomic molecule. Such oligomers would be stable in the gas phase and would likely react in a chemical ionization experiment to form HgOH$^+$. A less extensive absolute rate study of the reaction has also been reported by Sumner et al. (2005) who monitored Hg^0 removal in excess O_3. They estimated that 30-40% of the reacted Hg^0 was deposited to the wall and obtained a rate coefficient of $6.4\pm2.3\times10^{-19}$ cm^3 molecule^{-1} s^{-1}.

Accurate thermochemistry is critical in assessing this reaction and its potential role in atmospheric transformation of mercury. Hall reported a large negative free energy change for this reaction based on JANAF thermochemistry that assumes that HgO is bound by 268 kJ mol^{-1} and this thermochemistry is also cited by Pal and Ariya. However recent calculations on the electronic structure of HgO suggest that in fact it is a very weakly bound molecule. Tossell (2003) reported calculations on a series of possible reactions of HgO and found that HgO was unbound with respect to reactants while Shepler and Peterson (2003) reported that HgO was bound by approxinately17 kJ mol^{-1}. Shepler and Peterson discuss the prior experimental and theoretical calculations and make a convincing argument that the prior experimental evidence for a strongly bound diatomic HgO molecule is unconvincing. Using this new thermochemistry the atom transfer reaction (4a) becomes endothermic by approximately 90 kJ mole^{-1} with a large positive free energy for any reasonable standard entropy of HgO. We can consider the implications by calculating the free energy change and equilibrium constant based on the new thermochemistry. Using an HgO bond distance of 1.91Å we calculate a standard entropy of $S^0 = 239.0$ J K^{-1} mol^{-1} for HgO which is close to the JANAF value of 239.3 J K^{-1} mol^{-1}. We can use these values to calculate the free energy change and equilibrium constant for reaction (4a).

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

Using $\Delta H^0 = 93$ kJ mol^{-1} and $\Delta S^0 = 30$ J K^{-1} mol^{-1} we obtain $\Delta G^0 = 84$ kJ mol^{-1}

$$K = \exp(-\Delta G^0/RT) = 2.4 \times 10^{-15} \text{ at } 300 \text{ K}$$

Using the principle of detailed balance we can calculate the rate coefficient for reaction (-4a) as follows assuming the rate coefficient reported by Pal and Ariya (2004) is correct.
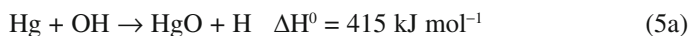
$$k_r = k_f /K = 7.5 \times 10^{-19}/2.4 \times 10^{-15} = 3.1 \times 10^{-4} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

This is at least six orders of magnitude faster than any physically reasonable rate coefficient, hence it is very unlikely that the oxidation of Hg by O_3 proceeds as a homogeneous gas phase reaction. Indeed HgO would have to be bound by at least 50 kJ mol^{-1} for the above rate coefficient to be consistent with a physically realistic value for reaction (-4a). There is some level of uncertainty associated with the quantum mechanical calculations because of the large number of electrons and the issue of incorporating relativistic effects, nevertheless it seems inconceivable that the error could be large enough to make the O atom transfer energetically favorable. Calvert and Lindberg (2005) suggest that reaction might proceed via an addition reaction to produce a weakly bound molecule with a binding energy of ~16 kJ mole^{-1}. Such an addition complex would have no exothermic dissociation routes but it might diffuse to the reaction walls. In more recent work Tossell (2006) has shown that, in contrast to the monomer, ring-type oligomers, i.e. $(HgO)_n$, are stable and their formation on surfaces should be facile. Tossell (2006) states that a stable van der Waals complex of Hg and O_3 exists but gives no value for a binding energy and also notes that the isomerization of this species to $OHgO_2$, as suggested by Calvert and Lindberg (2003), is unlikely since it is endothermic but again quantitative thermodynamic data is not provided. If the reaction does proceed in the gas phase it must be via the formation of a weakly bound complex that is likely reversible since no exothermic decomposition pathways are accessible. In the laboratory experiments such a complex could diffuse to the reactor surface to form solid mercuric monoxide, possibly via oligomer formation. Such a process would be energetically favorable because of the exothermicity of oligomer formation and the lattice energy associated with the formation of the solid. If the concentration of the complex were sufficiently high it might also undergo self-reaction in the gas phase to form $(HgO)_2$ and higher oligomers but this is unlikely if the complex is bound by less than 20 kJ mol^{-1}. The overall loss kinetics initiated by such a reversible addition process are analogous to those described above for the reaction of OH with CS_2 and will be extremely complex since the observed rate coefficient will be a composite of the elementary rate coefficients involved in the formation and decomposition of the adduct and other irreversible loss processes which in this case is most likely surface loss. If reaction is initiated by a reversible addition process it appears that the adduct does not react with water molecules since the rate coefficient showed no dependence on relative humidity in the study by Hall. The combination of complex gas phase kinetics coupled with contributions from heterogeneous reactions could certainly explain the very large differences in the rate coefficients obtained in the recent studies of this reaction. However oxidation based on such a mechanism is unlikely to be of any significance in the atmosphere. At typical atmospheric concentrations a very small fraction of the Hg^0 would be present as adduct and the chances of heterogeneous removal would not be significant. If we assume that quantum calculations are not correct and the rate coefficient measured by Pal and Ariya (2004) does produce HgO it has significant implications for global models and would imply that ozone is the main oxidant of Hg^0 in the atmosphere. We can calculate the rate of transformation of Hg^0 by O_3 in the following manner: If we take the rate coefficient measured by Pal and Ariya (2004), 7.5×10^{-19} cm^3 molecule^{-1} s^{-1}, we require concentrations of

both Hg^0 and O_3 in molecule cm^{-3}. Ozone concentrations are typically given as a mixing ratio in ppb (parts per billion), with a typical value of 40 ppb at sea level over much of the continental US. At one atmosphere pressure and 300 K, 40 ppb corresponds to an absolute concentration of approximately 10^{12} molecules cm^{-3}. Hg^0 concentrations are typically quoted as absolute values, but in ng m^{-3}, a unit that is not typically used by atmospheric chemists to designate trace gas concentrations. An Hg^0 concentration of 2 ng m^{-3} corresponds to approximately 6×10^6 molecules cm^{-3}. The ozone concentration is much larger than the Hg^0 concentration and the reaction will not perturb the O_3 concentration. We can define an Hg^0 "half life", $t_{1/2}$, with respect to reaction with O_3, which is the time required to reduce Hg^0 to 50% of its original concentration. This is given by $\ln(2)/(k*[O_3]) = \ln(2)/(7.5\times10^{-19} \times 1\times10^{12}) = 9.2\times10^5$ s, or approximately 10.6 days. It should be noticed that this number does not depend on the Hg^0 concentration so the time required to reduce the concentration to 25% of its original concentration is 2 $t_{1/2}$. Although photochemically active, ozone does not have a strong diurnal variation as is observed with the production of, for example, OH. However the limited observations of RGM with hourly temporal resolution suggest that its production shows a strong diurnal variation. Several recent global modeling studies have concluded that field observations are inconsistent with this reaction being the major oxidant of Hg^0. Bergan and Rohde (2001) used a global model to examine the sensitivity of global mercury concentrations and their seasonal variation to changes in the rate coefficient for this reaction. They concluded that the rate coefficient of Hall (1995) is too slow to explain observed atmospheric concentrations of Hg^0. They also examined the effect of using a faster rate coefficient and making O_3 the sole oxidant of Hg^0. Using a rate coefficient that produced realistic Hg^0 concentrations they found latitudinal and seasonal variations that were not consistent with observations. More recently Seigneur et al. (2006) examined the effect of using the Pal and Ariya (2004) rate coefficient in their global model and found that it gave surface concentrations that ranged from 0.3 to 1.2 ng m^{-3}. The half-life of Hg^0 was reduced from 9 months to approximately 11 days which appears unrealistic unless there are competing reactions which reduce $Hg^{(II)}$ compounds in the atmosphere, which are as yet unidentified.

14.3.2 $Hg^0 + OH$

Again our evaluation of potential pathways for this reaction is dependent on the thermodynamics of the HgO molecule. A direct atom transfer is endothermic using either the old or new binding energy of HgO.

$$Hg + OH \rightarrow HgO + H \quad \Delta H^0 = 415 \text{ kJ mol}^{-1} \qquad (5a)$$

$$Hg + OH + M \leftrightarrow HgOH + M \quad \Delta H^0 = -40 \text{ kJ mol}^{-1} \qquad (5b)$$

However it does appear that HgOH is weakly bound, with both Tossell (2003) and Goodsite et al. (2004) calculating binding energies of ~30 and

40 kJ mole^{-1} respectively and, if so, it will rapidly redissociate to reactants at atmospheric temperatures. Goodsite et al. (2004) calculate a forward addition rate of 3.2×10^{-13} cm^3 molecule^{-1} s^{-1} and a dissociation rate of $\sim$3200 s^{-1} at 300 K. Again the kinetic situation is similar to that of the reaction of CS$_2$ with OH where both the forward and reverse rate coefficients are about a factor of ten larger than those calculated for HgOH but the equilibrium constant is almost the same. Hence, in the absence of further reaction of HgOH, we expect the reactants and products will form an equilibrium mixture with no permanent removal of reactants.

Using the old (Chase, 1998) binding energy for HgO, reaction with O$_2$ would be energetically favorable generating HgO and HO$_2$.

$$HgOH + O_2 \rightarrow HgO + HO_2 \quad \Delta H^0 = 210 \text{ kJ mol}^{-1}$$

However, using the more recent binding energies of Shepler and Peterson (2003) or Tossell (2006), this reaction becomes strongly endothermic, with $\Delta H = 210$ kJ mol^{-1} based on the binding energy of Shepler and Peterson (2003).

There have been three experimental studies of this reaction utilizing both absolute and relative rate approaches. Sommar et al. (2001) used a relative rate technique monitoring the loss of Hg^0 relative to cyclohexane in the presence of OH generated by the photolysis of methyl nitrate. They reported four experiments in which mercury consumption was 3 to 5% of the starting concentration and reported a rate coefficient of $(8.7\pm 2.8) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}. Bauer et al. (2003) used a pulsed laser photolysis - pulsed laser induced fluorescence approach to monitor the decay of OH in a pseudo-first order excess of Hg^0 at room temperature and atmospheric pressure in both air and He buffer gases. They saw no evidence for reaction and reported an upper limit of $(1.2) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. These experiments have the time resolution to directly observe an equilibrium formation of HgOH and based on their failure to observe such an equilibrium they concluded that the equilibrium constant, K_c, for this reaction must be less than 5×10^{-16} cm^3 molecule^{-1}.

Pal and Ariya (2004) used a relative rate technique generating OH by photolysis of isopropyl nitrate and monitoring the loss of mercury relative to five reference compounds. Measurements relative to cyclohexane, n-butane and 2-methylcyclopropane gave rate coefficients of approximately 13×10^{-14} cm^3 molecule^{-1} s^{-1}, while experiments relative to ethane and cyclopropane gave rate coefficients of approximately 9.5×10^{-14} cm^3 molecule^{-1} s^{-1}. The authors suggest that the lower values are appropriate because the rate coefficients of the unknown and reference compounds are of similar magnitude. This should improve the precision of the measurements since the consumption of mercury is larger, however it cannot explain the difference between the sets of measurements, such differences may well be indicative of kinetic complications. Pal and Ariya (2004) made product measurements that were similar to those employed in their study of the reaction of ozone with Hg^0 and observed HgOH$^+$ in chemical ionization experiments.

As we have noted, thermodynamic considerations suggest this reaction must proceed via a complex mechanism involving reversible addition and unless the weakly bound HgOH reacts to form stable products then no reaction will be observed.

$$HgOH + X \rightarrow products$$
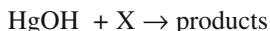
Since reaction with O_2 to form HgO is highly endothermic loss might occur via reaction with another radical species or wall loss. Sommar et al., (2001) suggest that "X" is O_2 and cite an endothermicity of ~ 30 kJ mol^{-1}, they suggest that the forward rate is measurable because of the low ratio of [HO$_2$] / [O$_2$], however this estimate of the endothermicity appears unrealistic. Pal and Ariya (2004) suggest that "X" may be O_2 or OH but do not discuss the implications of an addition mechanism for their measurements. Goodsite et al. (2004) have calculated rates for the forward and reverse reactions based on a binding energy of 39 kJ mol^{-1}. Calvert and Lindberg (2005) have discussed the measurements of Pal and Ariya (2004) and Sommar et al. (2001) and suggest that "X" is the sum of the potential reactants, {X = OH, HO$_2$, RO, RO$_2$, NO, NO$_2$} in the experiments. They assign a rate coefficient of 2.5×10^{-10} cm^3 molecule^{-1} s^{-1} to reaction, however in their simulations X is primarily the sum of [NO] plus [NO$_2$] which build up to significant concentrations and there is no experimental evidence or theoretical calculations to support such a rate or indeed to show that NOHgOH or NO$_2$HgOH are stable molecules. Calvert and Lindberg (2005) conclude that this reaction is probably unimportant in the actual atmosphere because the concentration of reactants that can remove HgOH will be low, making this an ineffective loss pathway.

Bergan and Rodhe (2001) used the rate coefficient reported by Sommar et al. (2001) as the sole oxidant for Hg^0 in their global model and concluded that it was a factor of three too large to be consistent with observations. However Seigneur et al. (2006) note that this model did not contain the aqueous phase reduction of Hg$^{(II)}$ by HO$_2$ and conclude that observations are consistent with a faster OH rate coefficient if the reduction path is occurring. Selin et al. (2007) also use the faster rate coefficient in their global model and conclude that this reaction is the dominant sink for Hg^0. None of these models incorporated bromine chemistry.

This reaction is the major route for the oxidation of Hg^0 in most current models so developing a clear understanding of the detailed mechanism of this reaction is critical. It seems clear that neither a direct atom transfer, nor an addition followed by reaction with O$_2$ would be energetically feasible. However, if the Goodsite et al.(2004) dissociation rate for HgOH is correct it has a lifetime of less than 1 ms at room temperature and reaction with O$_2$ would be the only feasible route for permanent loss of HgOH. It should be recognized that no reasonable, i.e. consistent with known thermochemistry, chemical mechanism has been proposed for the OH initiated oxidation of Hg^0 and it seems unlikely that this reaction contributes to the oxidation of Hg^0 in the atmosphere. Direct observation of the equilibration process and

measurements of the reactivity of HgOH are key in resolving the importance of this reaction. Relative rate studies using an OH source that is less susceptible to secondary chemistry and does not generate NO_x would also be very useful.

14.3.3   Halogen Reactions

14.3.3.1 Hg^0 + Cl

$$Hg^0 + Cl + M \rightarrow HgCl + M \qquad (6)$$

This reaction involves the three-body recombination of Hg^0 and Cl atoms and the rate coefficient would be expected to be pressure dependent and to exhibit a negative activation energy if expressed in Arrhenius form. This type of atom recombination involves the formation of an energized HgCl* molecule which, in the absence of collisions will redissociate to reactants. If the energized molecule undergoes a collision which removes enough energy to give a molecule below the dissociation threshold it will thermalize forming a stable HgCl molecule.

$$Hg + Cl \leftrightarrow HgCl*$$

$$HgCl* + M \rightarrow HgCl + M$$
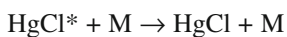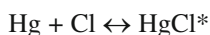
This reaction mechanism predicts that the reaction will show a distinct pressure dependence with an effective rate coefficient which is third order at low pressures, i.e. -d[Cl]/dt = k[Hg][Cl][M] and becomes pressure independent at high pressures. The transition from third to second order behavior is known as the fall-off region. For a typical atom-atom recombination we expect the reaction to be in the low pressure, third order regime at atmospheric pressure and below. The effective rate coefficient also depends on the identity of the "third body", M, as different sizes of M will differ in their efficiency in deactivating HgCl*. We expect atoms to be least efficient, and then deactivation efficiency to increase as we move from diatomic to more complex polyatomic molecules. Since the effective rate of reaction depends on the rate of deactivation we expect that the rate coefficient will increase as the temperature is lowered. As we lower the temperature the energy associated with translational motion of the reactants decreases hence less energy has to be removed from HgCl* to bring it below the dissociation threshold.

There have been three recent experimental studies of this reaction. Ariya et al. (2002) reported a relative rate study of this reaction. In initial experiments Cl atoms were produced by photolysis of trichloroacetylchloride in air. Five different reference molecules were used obtaining results, which differed by a factor of 270 in the measured relative rates together with a strong non-linearity of the relative rate plot. They concluded that the variation was caused by the presence of a secondary reaction between the reference molecules and OH. The buffer gas was switched from air to nitrogen to eliminate oxygen chemistry, giving an overall reduction in the observed

rate. However, the variation in the measured relative rate between the reference molecules was still a factor of 30 and the non-linearity remained. Ultimately, a series of 8 measurements were made using 1,3-dichloropropane as the reference molecule with the addition of 835 ppm of benzene as an OH scavenger. The reported rate coefficient, $(1.0 \pm 0.2) \times 10^{-11}$ cm^3 molecules^{-1} s^{-1}, was determined from this sub-set of the data.

Spicer et al. (2002) reported a relative rate study utilizing the photolysis of Cl$_2$ as a source of Cl atoms. They attempted to use both toluene and dimethyl sulfide as reference molecules but obtained inconsistent results with toluene. The experiments were performed in air containing 29 ppbv NO. The reason for the addition of NO was not specified. They derived a rate coefficient of 6.4×10^{-11} cm^3 molecules^{-1} s^{-1}. These experiments were performed in air and, as we discuss below, reaction of Cl atoms with O$_2$ could cause kinetic complications.

Donohoue et al. (2005) used a pulsed laser photolysis-pulsed laser induced fluorescence approach to measure the rate coefficient over a wide range of temperature and pressure. This type of system has been used extensively for the measurement of elementary rate coefficients that are important in atmospheric and combustion systems. Such experiments are typically performed under pseudo-first order conditions that require that one reactant is present in at least a factor of 10 excess in concentration relative to the other reactant. Normally the stable reactant in a radical molecule reaction is in excess. In such a configuration only the absolute concentration of the reactant that is present in excess is required to obtain a rate coefficient. The relative change in the concentration of the minor reactant is then monitored as a function of time to obtain the rate coefficient. The configuration of choice would be to monitor the variation in Cl atom as a function of time in an excess of mercury. The mercury concentration can be monitored photometrically with high precision and the variation in the Cl atom concentration can be monitored using laser-induced fluorescence. Using this approach Donohoue et al. (2005) were unable to see any evidence for reaction at room temperature. The low vapor pressure of mercury limits such an approach to fast reactions and the problem is exacerbated for studies that are attempting to measure the rate coefficient at low temperature. As an alternative approach, Donohoue et al. (2005) generated a large excess of Cl atoms by photolysis and monitored the decay of Hg^0. This approach makes the experiments more difficult to implement and complicates the data analysis. Since Cl atoms react via a recombination reaction it requires the temporal profile of both species to be monitored using LIF. Since the Cl atom concentration is changing as a function of time, the Hg^0 profiles do not show a simple exponential decay and rate coefficients are obtained by numerical integration to fit the observed Hg^0 temporal profiles. In addition the approach requires that the absolute concentration of Cl atoms is known accurately. This cannot be measured directly and has to be calculated from the concentration of Cl$_2$ and the photolysis laser flux. The advantage of this approach is that it allows the rate coefficient to be measured over a large temperature and pressure range and the effect of a change in the bath gas can be tested. In this case the results were consistent with expectations and the observed second order rate coefficients showed a linear dependence on pressure, a slightly negative temperature dependence and a significant difference in deactivation efficiency with N$_2$ and He as third bodies. Donohoue et al. (2005) give an expression that can

be used to calculate the recombination rate at any temperature and pressure in the troposphere. Their expression gives a rate coefficient of 5.4×10^{-13} cm^3 molecule^{-1} s^{-1} at 298 K and one atmosphere pressure in air.

The main uncertainty in this approach is the calculation of the absolute [Cl] and the authors discuss this in detail. One potential complication that Donohoue et al. (2005) did not discuss relates to the potential reaction of the HgCl product of the reaction with excess Cl atoms. They assumed this reaction proceeds via another three body recombination to form HgCl$_2$. Balabanov et al. (2005) have suggested that the analogous Br reaction can proceed via an alternative bimolecular route reforming Hg^0 atoms. For Cl this reaction would be:

$$HgCl + Cl \rightarrow HgCl_2 \qquad (7a)$$

$$\rightarrow Hg + Cl_2 \qquad (7b)$$

If reaction (7b) were significant then Hg^0 atoms would be regenerated and the experiments which monitored Hg^0 loss would underestimate the rate coefficient. Such a channel would not impact the experiments which were performed with Hg^0 in excess and this suggests (7b) is not significant.

Donohoue et al. (2005) discuss an additional issue that is relevant when these experiments are performed in air. Cl reacts with molecular oxygen to form a weakly bound adduct, ClO$_2$. This produces potential complications due to the reaction of Cl atoms with ClO$_2$. Donohoue et al. (2005) saw a large increase in the rate of loss of Cl atoms in the presence of O$_2$ that was consistent with the following chemistry.

$$Cl + O_2 + M \leftrightarrow ClO_2 + M$$
$$Cl + ClO_2 \rightarrow Cl_2 + O_2$$
$$\rightarrow 2ClO$$
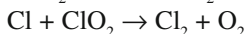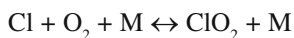
A significant enhancement in the apparent recombination rate coefficient of mercury and chlorine atoms was also observed in the presence of air. If this loss were solely due to the mercury chlorine recombination reaction it would have resulted in an increase in the recombination rate coefficient by a factor of 4 relative to the rate coefficient obtained in N$_2$. Again this is not consistent with the expected relative three body efficiencies of nitrogen and oxygen and they chose not to report a recombination rate coefficient for M = O$_2$. This observation suggests an additional loss of mercury atoms due to the secondary chemistry described above. Based on this chemistry the only plausible candidates are ClO or ClO$_2$. The most likely candidate is reaction with ClO$_2$.

$$Hg + ClO_2 \rightarrow HgCl + O_2$$
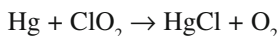
This reaction requires further investigation since the reaction is endothermic and, unlike the recombination reaction, no third body is required to stabilize the HgCl product.

Khalizov et al. (2003) calculated the recombination rate coefficient. They used electronic structure calculations to obtain both molecular parameters and the capture rate or high-pressure limit. They determined a pressure dependent rate coefficient by assuming strong collisional deactivation. This, typically unrealistic, assumption should produce the maximum possible recombination rate coefficient at any particular pressure. The value they obtained, 2.8×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K, 760 Torr, is a factor of three smaller than the rate coefficient reported by Ariya et al., (2002) a factor of twenty smaller than that reported by Spicer et al. (2002) and a factor of five faster that the rate coefficient reported by Donohoue et al. (2005). In the atmosphere chlorine atoms react rapidly with methane which limits their concentration. As a consequence concentrations are much lower than those of bromine atoms and this reaction is not significant in global models. Based on current models it also appears to be unimportant in polar mercury depletion events, but it may be a source of RGM in the marine boundary layer. An accurate determination of this rate is required for modeling purposes and the discrepancies in the experimental database need resolution. In addition the potential role of ClO$_2$ should be resolved as this could dramatically enhance the effective rate of the Cl reaction, especially at low temperatures where the stability of ClO$_2$ increases.

14.3.3.2   Hg^0 + Br

$$Hg^0 + Br + M \rightarrow HgBr + M \qquad (8)$$

This reaction has been studied in three recent experimental systems using both direct and relative rate techniques. As with the Cl atom reaction this is a standard three body recombination reaction. Ariya et al. (2002) performed a relative rate study using a single reference reaction, Hg^0 with 1- butene, to measure the relative rate of reaction. They obtained a rate coefficient of 3.2×10^{-12} cm^3 molecules^{-1} s^{-1} Kinetic studies on the reaction of Hg^0 and 1-butene are limited, with only one study referenced. This study was also a relative rate study and the observed rate coefficient depended on the O$_2$ partial pressure, indicating a complex reaction mechanism. In the Ariya et al. (2002) study the rate observed depended on the concentration of the reference molecule, the concentration of the OH scavenger, and the identity of the buffer gas. The observed rate coefficient for reaction varied by a factor of 3 as the buffer gas was varied between nitrogen and air. In order to obtain linear relative rate plots they added large amounts of an OH scavenger (cyclohexane) leading to an enhancement in the absorption of reactant on the cell walls. Ariya et al. (2002) reported that the primary complication to their system was enhanced removal of the reference compound by reaction with OH or loss on the cell walls.

Spicer et al. (2002) report a relative rate study monitoring Hg^0 loss relative to DMS and propene. They obtained rate coefficients of 3×10^{-13} cm^3 molecule^{-1} s^{-1} relative to DMS and 9×10^{-13} cm^3 molecule^{-1} s^{-1} relative to propene with the latter considered more reliable.

Donohoue et al. (2006) used a pulsed laser photolysis-pulsed laser induced fluorescence approach to measure the rate coefficient as a function of temperature and

pressure. As described above for their Cl atom study, they generated a large excess of Br atoms by photolysis and monitored the decay of Hg^0 and the same complications ensue. Both Br and Hg^0 profiles were monitored using LIF and rate coefficients were obtained by numerical integration to fit the observed Hg^0 temporal profiles. Again the approach requires that the absolute concentration of Br atoms is known accurately. The rate coefficient was measured over a large temperature and pressure range and the effect of a change in the bath gas was measured. The observed second order rate coefficients showed a linear dependence on pressure, a slightly negative temperature dependence and a significant difference in deactivation efficiency with N_2 and He as third bodies. Donohoue et al. (2006) give an expression that can be used to calculate the recombination rate at any temperature and pressure in the troposphere. Their expression gives a rate coefficient of 3.6×10^{-13} cm^3 molecule^{-1} s^{-1} at 298 K and one atmosphere pressure in air. As noted above, a significant reaction between HgBr and Br to regenerate Hg^0 could produce an underestimation of the rate coefficient in these experiments.
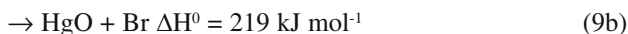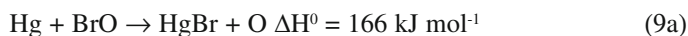
There have been three computational studies of this reaction, Khalizov et al. (2003) calculated the collision frequency or "capture rate" to form an energized HgBr* and assumed that every collision stabilizes the molecule forming HgBr. This "strong collision" assumption should give an upper limit to the rate coefficient since, in practice, not every collision will remove enough energy to deactivate HgBr*. They obtained a rate coefficient of 2.07×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K, 760 Torr. Goodsite et al. (2004) performed a more physically realistic calculation and obtained a rate coefficient of 1.1×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K, 760 Torr. They used a master equation approach and assumed an average energy transfer per collision of 400 cm^{-1}. However this energy transfer parameter is an estimate and is not based on experiment or a detailed calculation of the HgBr-N_2 potential. Shepler et al. (2007) used high level calculations to construct a global potential energy surface for HgBr + Ar and calculated the collisional dissociation rate using quasi-classical trajectories. The HgBr recombination rate was then calculated from detailed balance and they obtained a rate coefficient of 9.8×10^{-13} cm^3 molecule^{-1} s^{-1} at 298 K in 760 Torr of Ar buffer.

There have been *two* modeling studies that have examined the impact of the inclusion of this model in studies. Holmes et al. (2006) used kinetic data from Donohoue et al. (2006) and Goodsite et al. (2004) together with the global Br concentrations from the model of Yang et al. (2005) to model the global mean atmospheric lifetime of Hg^0. They concluded that reaction with Br atoms is a major and possibly the dominant global sink for Hg^0, with most of the oxidation taking place in the middle and upper troposphere. They also that noted that lack of kinetic data on the fate of HgBr is a major source of uncertainty in the model.

It is likely that this is a key reaction both in polar mercury depletion events and in the global Hg^0 oxidation cycle. Overall we see that the level of uncertainty is high relative to a typical atmospheric reaction but two very different experimental approaches and theoretical calculations give results that span less than an order of magnitude. For the purposes of atmospheric modeling we would suggest that

values between 1×10^{-12} and 3×10^{-13} are used to examine the effects of the uncertainty in this rate coefficient on model predictions. Additional studies are needed to reduce the uncertainty in this rate coefficient and to characterize the fate of HgBr, another key parameter in models.

14.3.3.3   Hg + BrO

$$Hg + BrO \rightarrow HgBr + O \quad \Delta H^0 = 166 \text{ kJ mol}^{-1} \tag{9a}$$

$$\rightarrow HgO + Br \quad \Delta H^0 = 219 \text{ kJ mol}^{-1} \tag{9b}$$

There have been two experimental determinations of the rate coefficient using relative rate techniques. Spicer et al. (2002) used photolysis of Br_2 in the presence of O_3 to produce BrO and monitored the loss of Hg^0 relative to the loss of dimethyl sulfide. They reported the results of three experiments which ranged from 3.0 - 6.4 $\times 10^{-14}$ cm^3 molecule^{-1} s^{-1}. Raofie and Ariya (2003) also report a relative rate measurement using photolysis of bromine and dibromomethane in the presence of O_3 to produce BrO. The monitored Hg^0 loss relative to three reference molecules, propane, butane and DMS and reported upper and lower limits of 1×10^{-13} and 1×10^{-15} cm^3 molecule^{-1} s^{-1} for the rate coefficient. They also performed a product study again using photolysis of bromine and dibromomethane in the presence of O_3 to produce BrO (Raofie and Ariya, 2004). They reported observation of HgBr, HgO, and HgOBr / HgBrO. In all of these experiments BrO would be photolyzed and there would be a steady state concentration of Br atoms which would react with Hg^0. Calculation of the Br atom concentration requires a knowledge of the photolysis rate but this is a potential source of secondary chemistry in these studies. It is clear that the thermodynamics of this reaction are not consistent with an abstraction reaction to form HgBr or HgO, however calculations suggest that the addition complex HgBrO is bound by 84 kJ mol^{-1}. It seems unlikely that this reaction can play a role in mercuy transformation via reactions 9a or 9b. Studies on the stability of the addition complex and its potential reactions are necessary to assess the importance of this channel.

14.3.3.4   Hg^0 + NO$_3$

$$Hg + NO_3 \rightarrow HgO + NO_2 \quad \Delta H^0 = 195 \text{ kJ mol}^{-1} \tag{10}$$
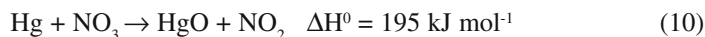
There has been a single reported measurement of this reaction by Sommar et al. (1997) using a discharge flow technique. The authors report an exothermicity of -12 kJ mol^{-1} for this reaction based on the old HgO thermochemistry. Again the new thermochemistry makes this reaction sufficiently endoergic that the possibility of the atom transfer can be dismissed. The reported experiments measured a heterogeneous

wall reaction at two surface-to-volume (S/V) ratio's, 7.6 and 4.0×10^{-14} cm^3 molecule^{-1} s^{-1} and then extrapolated to S/V = 0 to extract a gas phase component of 4.0×10^{-15} cm^3 molecule^{-1} s^{-1}, a factor of ten slower than the slowest measured rate coefficient. They acknowledged that "In practice, the stated rate coefficient should be taken as an upper limit for the reaction between Hg and NO$_3$". The endothermicity of this reaction is such that it cannot proceed at a measurable rate in the gas phase and it will not be significant in the atmosphere, even at night in polluted atmospheres.

14.4   Gas Phase Oxidation: Issues and Uncertainties

It is clear that that the limited amount of laboratory data on mercury reaction kinetics makes it difficult to provide a definitive evaluation of published rate coefficients. No data exists on reaction with I or IO although again the calculations of Goodsite et al. (2004) suggest that HgI is weakly bound and will rapidly dissociate to Hg^0 and I. Based on this evaluation of the laboratory data, thermodynamics and models we would suggest that reaction of Hg^0 with Br and possibly BrO are likely to explain both the localized dramatic loss of Hg^0 during mercury depletion events and the global oxidation of Hg^0 in the troposphere. Currently there are no published data on the reactions of HgBr and this is a key uncertainty. To constrain models independent measurements of key rates that agree within a factor of two or better are required. In addition field measurements showing the vertical profiles of both Hg^0 and RGM together with speciated measurements of RGM would do much to resolve these issues.

14.5   Mercury Chemistry in the Atmospheric Aqueous Phase

The aqueous phase chemistry of Hg in the atmosphere involves redox reactions, complexation and phase exchange equilibria and while occurring mostly in cloud droplets, can also take place in deliquesced aerosols. In terms of the amount of water present (atmospheric liquid water content) the most important atmospheric aqueous phase is cloud water. The liquid water content associated with deliquesced aerosol particles is orders of magnitude lower, but their specific chemical composition and the high concentrations of some chemical species make them relevant in terms of the atmospheric aqueous phase chemistry of Hg.

14.5.1   Redox reactions

Elemental mercury is not highly soluble it has a Henry's Law constant of 1.1×10^{-1} M atm^{-1} (Sanemasa, 1975) and its concentration in the atmospheric aqueous phase reaches a stable value in a matter of minutes. Once in the aqueous phase Hg can be oxidized by a number of compounds present in the droplet. The most important of

these in cloud water is ozone (Munthe, 1992; Iverfeldt and Lindqvist, 1986) on account of its relative abundance and the rate constant for the $Hg^0_{(aq)} + O_{3(aq)}$ reaction. Other aqueous phase reactions which oxidize Hg^0 are those with the hydroxyl radical (OH), (Lin and Pehkonen, 1997; Gardfeldt et al., 2001), HOCl/OCl⁻ (Lin and Pehkonen, 1998), and the most recently identified, the reaction with Br₂/HOBr/OBr⁻ (Wang and Pehkonen, 2004). The aqueous phase reactions of Hg which have been studied to date are shown in Table 14.1.

The reduction of oxidized Hg compounds ($Hg^{(II)}$) depends on the complex which Hg has formed in solution. Munthe et al. (1991) first investigated the reduction of Hg via complexation with the sulphite ion, SO_3^{2-}, and obtained a first order rate constant of 0.6 s⁻¹. This reaction was studied again by van Loon et al. (2000), who found a rate constant more than an order of magnitude slower, 0.0106 s⁻¹. Photolytic

Table 14.1   Aqueous phase reactions of Hg

Mercury Reactions and Equilibria	k or K (298K)	Reference
$Hg^0_{(aq)} + O_{3(aq)} \rightarrow HgO_{(aq)}$	4.7×10^7 M⁻¹s⁻¹	Munthe (1992)
$HgO_{(aq)} + H^+_{(aq)} \rightarrow Hg^{++}_{(aq)} + OH^-_{(aq)}$	1×10^{10} M⁻¹s⁻¹	Pleijel and Munthe (1995)
$Hg^{++}_{(aq)} + OH^-_{(aq)} \leftrightarrow HgOH^+_{(aq)}$	3.9×10^{10} M⁻¹	Pleijel and Munthe (1995)
$HgOH^+_{(aq)} + OH^-_{(aq)} \leftrightarrow Hg(OH)_{2(aq)}$	1.6×10^{11} M⁻¹	Pleijel and Munthe (1995)
$HgOH^+_{(aq)} + Cl^-_{(aq)} \leftrightarrow HgOHCl_{(aq)}$	2.7×10^7 M⁻¹	Pleijel and Munthe (1995)
$Hg^{++}_{(aq)} + Cl^-_{(aq)} \leftrightarrow HgCl^+_{(aq)}$	5.8×10^6 M⁻¹	Pleijel and Munthe (1995)
$HgCl^+_{(aq)} + Cl^-_{(aq)} \leftrightarrow HgCl_{2(aq)}$	2.5×10^6 M⁻¹	Pleijel and Munthe (1995)
$HgCl_{2(aq)} + Cl^-_{(aq)} \leftrightarrow HgCl_{3(aq)}^-$	6.7 M⁻¹	Clever et al. (1985)
$HgCl_{3(aq)}^- + Cl^-_{(aq)} \leftrightarrow HgCl_{4(aq)}^{--}$	13 M⁻¹	Clever et al. (1985)
$Hg^{++}_{(aq)} + Br^-_{(aq)} \leftrightarrow HgBr^+_{(aq)}$	1.1×10^9 M⁻¹	Clever et al. (1985)
$HgBr^+_{(aq)} + Br^-_{(aq)} \leftrightarrow HgBr_{2(aq)}$	2.5×10^8 M⁻¹	Clever et al. (1985)
$HgBr_{2(aq)} + Br^-_{(aq)} \leftrightarrow HgBr_{3(aq)}^-$	1.5×10^2 M⁻¹	Clever et al. (1985)
$HgBr_{3(aq)}^- + Br^-_{(aq)} \leftrightarrow HgBr_{4(aq)}^{--}$	23 M⁻¹	Clever et al. (1985)
$Hg^{++}_{(aq)} + SO_{3(aq)}^{--} \leftrightarrow HgSO_{3(aq)}$	2.1×10^{13} M⁻¹	Van Loon et al. (2001)
$HgSO_{3(aq)} + SO_{3(aq)}^{--} \leftrightarrow Hg(SO_3)_{2(aq)}^{--}$	1.0×10^{10} M⁻¹	Van Loon et al. (2001)
$HgSO_{3(aq)} \leftrightarrow Hg^0_{(aq)} + products$	T×exp((31.971×T)-12595)/T s-1	Van Loon et al. (2001)
$Hg^0_{(aq)} + OH_{(aq)} \rightarrow Hg^+_{(aq)} + OH^-_{(aq)}$	2.0×10^9 M⁻¹ s⁻¹	Lin and Pehkonen (1997)
$Hg^+_{(aq)} + OH_{(aq)} \rightarrow Hg^{++}_{(aq)} + OH^-_{(aq)}$	1.0×10^{10} M⁻¹ s⁻¹	Lin and Pehkonen (1997)
$Hg^+_{(aq)} + O_{2(aq)}^- \rightarrow Hg^+_{(aq)} + O_{2(aq)}$	1.1×10^4 M⁻¹ s⁻¹	Pehkonen and Lin (1997)
$Hg^{II}_{(aq)} + HO_{2(aq)} \rightarrow Hg^+_{(aq)} + O_{2(aq)} + H^+_{(aq)}$	1.1×10^4 M⁻¹ s⁻¹	Pehkonen and Lin (1997)
$Hg^+_{(aq)} + O_{2(aq)}^- \rightarrow Hg_{(aq)} + O_{2(aq)}$	fast	Pehkonen and Lin (1997)
$Hg^+_{(aq)} + HO_{2(aq)} \rightarrow Hg^0_{(aq)} + O_{2(aq)} + H^+_{(aq)}$	fast	Pehkonen and Lin (1997)
$Hg^{II}_{(aq)} + O_{2(aq)}^- \rightarrow Hg^+_{(aq)} + O_{2(aq)}$	0	Gårdfeldt, and Jonsson (2003)
$Hg^{II}_{(aq)} + HO_{2(aq)} \rightarrow Hg^+_{(aq)} + O_{2(aq)} + H^+_{(aq)}$	0	Gårdfeldt, and Jonsson (2003)
$Hg_{(aq)} + HOCl_{(aq)} \rightarrow Hg^{++}_{(aq)} + Cl^-_{(aq)} + OH^-_{(aq)}$	2.09×10^6 M⁻¹ s⁻¹	Lin and Pehkonen (1999)
$Hg_{(aq)} + ClO^-_{(aq)} \rightarrow Hg^{++}_{(aq)} + Cl^-_{(aq)} + OH^-_{(aq)}$	1.99×10^6 M⁻¹ s⁻¹	Lin and Pehkonen (1999)
$Hg_{(aq)} + HOBr_{(aq)} \rightarrow Hg^{++}_{(aq)} + Br^-_{(aq)} + OH^-_{(aq)}$	0.279 M⁻¹ s⁻¹	Wang and Pehkonen (2004)
$Hg_{(aq)} + OBr^-_{(aq)} \rightarrow Hg^{++}_{(aq)} + Br^-_{(aq)} + OH^-_{(aq)}$	0.273 M⁻¹ s⁻¹	Wang and Pehkonen (2004)
$Hg_{(aq)} + Br_{2(aq)} \rightarrow Hg^{++}_{(aq)} + 2Br^-_{(aq)} + OH^-_{(aq)}$	0.196 M⁻¹ s⁻¹	Wang and Pehkonen (2004)
$Hg^0_{(g)} \leftrightarrow Hg^0_{(aq)}$	0.13 M atm⁻¹	Schroeder and Munthe (1998)
$HgO_{(g)} \leftrightarrow HgO_{(aq)}$	2.69×10^{12} M atm⁻¹	Schroeder and Munthe (1998)
$HgCl_{2(g)} \leftrightarrow HgCl_{2(aq)}$	2.75×10^6 M atm⁻¹	Schroeder and Munthe (1998)
$HgBr_{2(g)} \leftrightarrow HgBr_{2(aq)}$	2.75×10^6 M atm⁻¹	Schroeder and Munthe (1998)

reduction of $Hg(OH)_2$ also occurs in solution, but not at a rate which is important in the atmospheric aqueous phase, (Xiao et al., 1994; Lin and Pehkonen, 1998b). The reduction of $Hg^{(II)}$ (independent of speciation) via a two step mechanism involving HO_2 was proposed by Pehkonen and Lin (1998), with the first reduction step to Hg^I having a rate constant of 1.1×10^4 M^{-1} s^{-1}, in the presence of chloride ions (otherwise 1.7×10^4 M^{-1} s^{-1}). However, whether this mechanism can occur in the atmosphere was called into question by Gardfeldt and Jonsson (2003), who suggested that the Hg^I formed in the first step of the reduction mechanism would be rapidly oxidized by dissolved O_2 ($k >> 10^9$ M^{-1} s^{-1}) before the second reduction step to elemental Hg could take place. This question is discussed more fully below.

14.5.2 Does Reduction Actually Occur in the Aqueous Phase?

The reaction between $Hg^{(I)}$ and dissolved O_2 (Nazhat and Asmus, 1973) is the reaction which is missing in the vast majority of atmospheric Hg models. It is potentially fundamental for two reasons: firstly if the oxidation of Hg^0 by OH proceeds as a two step reaction, as proposed by Pehkonen and Lin (1998), then there is no need to consider the second step as a rapid reaction between $Hg^{(I)}$ and OH, because long before $Hg^{(I)}$ encounters a second OH radical it will have already been oxidized by O_2. In fact in some reaction schemes this reaction is considered as $Hg^0 + OH$ leading directly to $Hg^{(II)}$, see Lin et al. (2006), which would appear to be a reasonable approximation. Secondly, the proposed reduction of all $Hg^{(II)}$ complexes by HO_2 proceeds via the formation of $Hg^{(I)}$ (Pehkonen and Lin, 1998), which then needs to react again with yet another HO_2 radical in order to be further reduced to $Hg^{0\cdot}$. If this is the case then the reaction is of absolutely no relevance whatsoever under atmospheric conditions because the chances of $Hg^{(I)}$ encountering a second HO_2 before it encounters a dissolved O_2 molecule are so small as to be irrelevant. Having said this, for the most part Hg models, from zero dimensional box models, to regional and global models include the reduction of $Hg^{(II)}$ by HO_2 in their reaction mechanisms without including the oxidation of $Hg^{(I)}$ by O_2. In many cases the reaction is assumed to proceed very rapidly after the initial reduction to $Hg^{(I)}$, so that some reaction schemes include this reaction as a direct reduction of $Hg^{(II)}$ to Hg^0, which, apart from being kinetically inaccurate leads to an overestimation of the reduction rate. If the reaction between $Hg^{(I)}$ and O_2 is included then the $Hg^{(II)} + HO_2$ reduction reaction becomes redundant in reaction schemes because the amount of $Hg^{(II)}$ reduced by sequential reactions with HO_2 is negligible.

14.5.3 Speciation

$Hg^{(II)}$ in solution can form complexes with a large number of ligands present in the atmospheric aqueous phase. The equilibrium constants for complex formation are

shown in table 14.1, which complexes will actually be present in solution depends on the abundance of the appropriate ligands and the pH of the droplets. The composition of droplets has been studied using both kinetic (where the equilibria are represented as forward and backward reactions) and equilibrium models, (Lin and Pehkonen, 1997; 1998; Pirrone et al. 2000). It is generally agreed that organic ligands are in too short supply to have any influence, and that in the presence of chloride the major part of the Hg$^{(II)}$ present in droplets is present as $HgCl_2$. Some concentrated solutions, such as occur when soluble atmospheric aerosols reach deliquescence may not follow this generalization, however they represent a very small proportion of the atmosphere's liquid water content. The marine sea salt aerosol is however potentially important in the atmospheric Hg cycle and is discussed separately below.

14.5.4   Is Aqueous Phase Chemistry Important Compared to Gas Phase Oxidation?

Measurements of Hg in precipitation have made it clear that wet deposition is in many areas the most important route by which atmospheric Hg enters terrestrial and aquatic ecosystems. It is also well known that Hg once oxidized in the gas phase is readily scavenged by cloud droplets, because the two compounds which are usually assumed to be formed, HgO and $HgCl_2$ are much more readily soluble that elemental Hg, the Henry's Law constant for $HgCl_2$ is 1.4×10^6 M atm^{-1} (Lindqvist and Rodhe, 1985), and that of HgO 2.75×10^6 M atm^{-1} (Schroeder and Munthe, 1998). The exception to this are the Marine Boundary Layer (MBL) and Arctic / Antarctic mercury depletion events, where a significant part of the oxidized Hg in the gas phase probably contains Br. Whether the oxidized Hg present in rain and cloud water is predominantly due to gas phase oxidation followed by scavenging or to Hg oxidation in the aqueous phase can be evaluated using photochemical box models.

The AMCOTS box model (Hedgecock et al., 2005) has been used to investigate the proportion of gas phase to aqueous phase oxidation of Hg in clouds. The model, which has been used up to now to study the influence of non-sea-salt sulphate and sea salt aerosol on Hg chemistry in the MBL has been adapted to include just one atmospheric aqueous phase, the cloud droplets, and the definition of the aqueous phase in terms of liquid water content, droplet radius and droplet number density changed to reflect the properties of different types of clouds. Simulating clean and polluted continental cumulus and marine stratus and cumulostratus clouds it was found that aqueous phase oxidation accounted for between 2 and 30% of all Hg oxidation. The major factors which influenced the proportion of Hg oxidized in the droplets are temperature, droplet number, cloud optical depth and time of day. The lower the temperature the higher the solubility of the gas phase species and therefore higher concentrations of reactants are found in the drops. The influence of droplet number was shown by comparison of polluted continental cumulus and maritime stratus clouds, in both cases a liquid water content of 0.3 g m^{-3} was used.

The maritime cloud has fewer and larger droplets (ND = 80) compared to the continental cloud (ND = 1300), the percentage of total oxidation which took place in cloud water was almost double in the continental cloud. The period during which aqueous phase oxidation is found to be most important is the night, and when the optical depth of the cloud is such that O_3 photolysis is severely reduced restricting the production of OH. Photolytically produced OH is responsible for a large part of the total oxidation during the day, but clearly has little influence during the hours of darkness. Simulating a polluted continental cumulus cloud ozone accounted for 65% of all the oxidation occuring, 35% of the total occuring in the gas phase and 30% in the aqueous phase.

Clearly then Hg chemistry in clouds is important and oxidized Hg compounds in rain come from both scavenging of RGM and in-droplet oxidation. Interestingly the proportion of in-droplet oxidation due to the reaction with O_3 never dropped below 95% in these simulations, and was usually between 98 and 99.9%. It would be worth investigating this finding further in regional models as the simplification of the aqueous phase reaction scheme could lead to savings in calculation times.

14.5.5   The Sea Salt Aerosol

Marine aerosols have been studied primarily because as they become acidified by the uptake of acidic gases they can release reactive halogen containing compounds to the atmosphere. This process is of interest to atmospheric chemists in general, particularly due to these halogen compounds potential for reaction with ozone and volatile organic compounds. It is also of potential significance in the cycling of Hg in the atmosphere as this process in a sense mimics the 'bromine explosion' seen in the Arctic at polar dawn. The concentrations of reactive halogens in the MBL does not reach the levels seen in the Arctic, but given that two thirds of the Earth's surface is water the spatial scale of this phenomena is important. Reactive halogen compounds, particularly those containing Br readily oxidize Hg, see above, and as oxidized Hg compounds are scavenged by droplets there is potential for the sea salt aerosol to contain relatively high concentrations of Hg. On top of this there is the composition of the aerosol themselves to be considered, the very high concentrations of chloride allow Hg to form complexes which are not formed in other atmospheric aqueous phases, such as $HgCl_3^-$ and $HgCl_4^{2-}$ (Hedgecock and Pirrone, 2001; 2004). The ability of the aerosol to 'carry' Hg increases dramatically as its chloride content increases (Pirrone et al., 2000). Modeling studies have also shown that the aerosol could process Hg which has been oxidized by O_3 or OH to give HgO. HgO is very readily scavenged and once in the aqueous phase reacts with H^+ to give an $Hg^{(II)}$ ion which in turn complexes with available ligands. The concentration of the chloride ion is such that the concentration of $HgCl_2$ in solution can increase until it is no longer in equilibrium with the concentration of $HgCl_2$ in the gas phase and therefore outgases from the aerosol.

14.6 The Uncertainty due to Hg Chemistry in Atmospheric Models

The uncertainty which results from the atmospheric processes which are included in atmospheric Hg modeling studies has been studied by Lin et al. (2006). Their article discusses the uncertainties relating to gas and aqueous phase chemistry as well as the other important factors such as emission speciation and dry and wet deposition parameterizations. They conclude that:

> *"Of the greatest importance for reducing model uncertainties is the accurate quantification of the reaction kinetics of mercury transformation mechanisms in both gas and aqueous phases. Thecurrent understanding of atmospheric mercury chemistry and related kinetics are based on the extrapolation of limited laboratory investigations. The appropriateness of such extrapolation has been questioned (e.g., Calvert and Lindberg, 2005, Gardfeldt and Jonsson, 2003). In addition, some of the reaction kinetics and products are not clearly defined. Since chemistry is the most important driving force for mercury deposition in regions away from the anthropogenic sources, further experimental investigations address-ing these kinetic and product uncertainties will greatly improvemodel performance in predicting both dry and wet depositions."*

They continue, mentioning the lack of data relating to adsorption isotherms for Hg and its compounds both for particulate matter in the gas phase and that included in cloud and rain droplets.

It is probably safe to say that the uncertainty in Hg chemistry lies less with the aqueous phase than with the gas phase and the adsorption of Hg and its com-pounds to solid particulates, especially in light of the box modeling tests mentioned above, from which it appears that by far the most important aqueous oxidant is O_3.

It must be pointed out however that there has only been one determination of the $Hg + O_3$ reaction rate constant in the aqueous phase and that the reduction reaction generally considered to be the most important might not actually occur at all. The last point raises a number of difficulties because observations quite clearly indicate a relatively long lifetime for atmospheric elemental Hg, but if indeed the reduction of $Hg^{(II)}$ by HO_2 is not pertinent to atmospheric aqueous phase chemistry there are no known reactions which reduce $Hg^{(II)}$ in the atmosphere at a rate which could offset all the oxidation which is believed to be occurring, so that the observed lifetime of Hg is essentially unexplainable in terms of the known reactions which occur in the atmosphere.

14.7 Deposition Processes

After emission mercury is subject to physical and chemical processes in the atmos-phere which may lead to conversion into the RGM form which is more soluble, adsorption to particles or ultimately some type of deposition, where its low volatility can lead to re-emission. The enhanced solubility of RGM compared to GEM will

lead to relatively quicker deposition, generally closer to sources, whereas GEM may be transported globally with a lifetime of approximately 1 year on average. GEM, RGM and TPM are eventually deposited by wet or dry deposition. What is known with relative certainty is that divalent mercury is much efficiently removed from the troposphere via wet deposition than elemental mercury due to its solubility. Gaseous and particulate forms of mercury are much more likely removed via dry deposition processes.

The deposition of RGM and GEM have been measured over various surfaces with chamber and micrometeorological techniques (Edwards, et al., 2001; Skov et al., 2006; Cobbett and Van Heyst, 2007) with varying results. Deposition has also been modeled (Steffen et al., 2007). Cobbett et al. (2007), summarize their own flux measurements of GEM, RGM and TPM over an arctic sampling site and review the published flux data for the ten years previous to their study. None of the studies have yet documented the causal effect that the observations of mercury deposited end up in the Arctic food chain. Though a reasonable hypothesis, observational data shows that under proper conditions, the mercury could be reemitted to the atmosphere. More studies are needed to ultimately describe the mass balance and fate of mercury in the Arctic.

Is it possible to identify regions that are most sensitive? Mercury has been investigated in all regions of the world, see previous chapters. There is general agreement in the literature that similar trends are noted in the northern hemisphere. Data from the southern hemisphere is more limited but note similar depositional trends and similar preanthropogenic natural background levels when compared to the northern hemisphere (Steffen et al., 2007).

Peatlands under the proper conditions can be used to investigate the environmental record of mercury deposition (Madsen, 1981). In general, the "natural" or pre anthropogenic rate of deposition for mercury, based on a rough approximation of all various environmental archives for example: ice cores, lake and marine sediments and peat sediments is on the order of 2 μg m^{-2} per yr^{-1}, depending on the archive and site (Givelet et al., 2003). This amount generally increases with a factor of three to ten through the anthropogenic peak, and has been falling since then. The peak has been seen in the 1990s or in the 1950s. What will happen to the mercury in the peatlands with increased warming and the hydrological changes with accompanying biological activity this will entail is pure conjecture. Never the less, peatlands represent significant natural sinks of mercury that could be mobilized in the next 50 years.

Swain et al. (1992) investigated whole-basin mercury fluxes, determined from lake-wide arrays of dated sediment cores. The analyses indicated that the annual deposition of atmospheric mercury increased from 3.7 to 12.5 μg m^{-2} (1990) since 1850, with the last decades showing a decline. 25 percent of atmospheric mercury deposition to the terrestrial catchment was exported to the lake. The deposition increase was similar among sites, implying regional or global sources for the mercury entering these lakes.

Peat records from the Faroe Islands in the North Atlantic had average rate of atmospheric Hg accumulation from 1520 BC to AD 1385 of 1.27 ± 0.38 μg m^{-2} yr^{-1}.

Br and Se concentrations and the background Hg/Br and Hg/Se ratios were used to calculate the average rate of *natural* Hg accumulation for the same period of 1.32 ± 0.36 µg m^{-2} yr^{-1} and 1.34 ± 0.29 µg m^{-2} yr^{-1}, respectively (Shotyk et al., 2005).

The total mercury fluxes were similar to the preanthropogenic rates obtained using peat cores from Switzerland, southern Greenland, southern Ontario, Canada, and the northeastern United States (Givelet et al., 2003; 2004; Shotyk et al., 2003; 2005; Roos-Barraclough and Shotyk, 2003; Roos-Barraclough et al., 2006). Values on the Faroe Islands were representative of those measures at other sites on the northern hemisphere in similar studies. On the Faroe Islands, the maximum rate of Hg accumulation was 34 µg m^{-2} yr^{-1}. The greatest fluxes of anthropogenic Hg accumulation calculated using Br and Se, respectively, were 26 and 31 µg m^{-2} yr^{-1}. The rate of atmospheric Hg accumulation in 1998 of 16 µg m^{-2} yr^{-1} was comparable to the values recently obtained by atmospheric transport modeling for Denmark, the Faroe Islands, and Greenland (Shotyk et al., 2005).

Environmental archives in the above studies already show a decreasing load of mercury in the past decade, likely due to reductions in emissions from the power industry (due to better emission controls for many other types of pollutants that likely inhibit much of the emission of mercury), though many more experiments are needed in this area as well, and fall in post eastern block industrial activity decreased emissions. The actual reduction in loadings have not been calculated or modelled as it is not a simple linear relationship, since warming climate will likely increase mercury emissions from previously deposited mercury.

Although many archives have been investigated, there is still poor geographic resolution in both hemispheres. The transfer functions which describe the mass transfer between the atmosphere and the surface of the archive needs to be further studied for all archives as do possible physical, chemical and biological perturbations which might be affecting the accuracy of the records. The records of mercury deposition are only as good as their chronology and advances in high resolution dating should continue to be made. Archives that have been investigated for mercury should be reanalyzed to establish a climate proxy and these records should be compared, as relatively few records exist that both contain historical mercury and climate proxy records.

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