Chapter-13

MODELLING CHEMICAL AND PHYSICAL PROCESSES OF HG COMPOUNDS IN THE MARINE BOUNDARY LAYER

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INTRODUCTION

Only five years ago a chapter in a book such as this with the above title would either have been extremely short, or simply not included. The inclusion of this chapter is evidence of the progress made in fields as diverse as analytical methods and instrumentation, chemical kinetics and atmospheric chemistry modelling, as well as of the ever increasing interest in mercury (Hg) within both the scientific and environmental policy communities. The reason for the current interest in Marine Boundary Layer (MBL) processes and their influence on Hg was the discovery of higher than expected concentrations of Reactive Gaseous Mercury (RGM or RGHg or $Hg^{II}_{(g)}$) at coastal sites (Mason et al., 2001, Wangberg et al., 2001) and in the MBL of both seas (Sprovieri et al., 2003) and oceans (Mason et al., 2001, Laurier et al., 2003). The $Hg^{II}_{(g)}$ concentration was also found to vary diurnally with a maximum occurring with maximum solar radiation intensity and a minimum at night. $Hg^{II}_{(g)}$ is not a single compound, it is an operationally defined quantity which refers to the oxidised inorganic mercury compounds present in the gas phase which are collected on KCl denuders, see chapter 7. The most probable components of $Hg^{II}_{(g)}$ are $HgCl_2$ and $HgBr_2$, possibly with HgO and $Hg(OH)_2$. $Hg^{II}_{(g)}$ is fundamental to Hg cycling because its chemical and physical characteristics differ so greatly from those of $Hg^{0}_{(g)}$. Where $Hg^{0}_{(g)}$ is volatile and sparingly soluble, the compounds which make up $Hg^{II}_{(g)}$ are far less volatile and far more soluble,

thus Hg deposition is almost totally dominated by $Hg^{II}_{(g)}$ whilst Hg emission, even industrial emission, is predominantly $Hg^0_{(g)}$. Modelling studies had suggested that the sea salt aerosol could be important in Hg cycling in the MBL because of its ability to form a range of Hg^{II} complexes due to its high chloride ion content (Pirrone et al., 2000). Further modelling studies suggested that Hg^{II} produced in the gas phase (Hg^0 from the reaction of Hg^0 + O_3) could be scavenged and then cycled via the sea salt aerosol to $HgCl_2$, which is more volatile than HgO, thus providing an MBL source of $Hg^{II}_{(g)}$, (Hedgecock and Pirrone, 2001).

The development of our understanding of Hg chemical and physical processes in the MBL, is intertwined with the study of Hg in the Arctic, and has gained very much from the study, both in the field and modelling, of tropospheric O_3 in remote areas, specifically the Arctic and the remote MBL.

Taking things in chronological order, it was in the late 80s that ozone depletion events were first reported during polar spring, (Bottenheim et al, 1986), these events were linked to photochemical processes, (Barrie et al., 1988). In the years that followed there were a number of field and theoretical investigations into the mechanism behind the rapid O_3 destruction, which pointed to the involvement of bromine containing radicals, (Fan and Jacob, 1992, Barrie and Platt, 1997, Foster et al, 2001). Measurements of $Hg^0_{(g)}$ over a number of years at Alert in Canada showed that when O_3 depletion events occurred, the concentration of $Hg^0_{(g)}$ also decreased rapidly, often to below the detection limit of the measurement techniques employed (Schroeder et al, 1998). This observation led to the suggestion that it was likely to be the Br radical compounds which were responsible for the Hg depletion events. At around the same time model studies were performed to see what effect, if any, the halogen radical chemistry seen in the Arctic may have in the MBL, (Vogt et al, 1996, Sander and Crutzen, 1996). Model predictions suggested that halogen compounds (Br_2 and BrCl) would be released to the atmosphere as a result of the acidification of the sea salt aerosol, and that the radicals produced by their photolysis would destroy O_3.

Since then the phenomenon known as 'Sunrise Ozone Destruction' has been observed in the sub-tropical Pacific (Nagao et al., 1999), and a number of studies have observed depletion of Br containing species in supermicrometer sea-salt aerosol, and enrichment of the same species in submicron marine aerosol, (Sander et al., 2003). The link between O_3 destruction at polar dawn with $Hg^0_{(g)}$ depletion and the measurement of elevated RGM concentrations in marine air masses hinted that Hg^0 oxidation processes were also at work in the MBL. The recent measurement of the reaction rates of $Hg^0_{(g)}$ + $OH_{(g)}$ (Sommar et al., 2001) and subsequently of $Hg^0_{(g)}$ + $Br_{(g)}$ (Ariya et al., 2002), have been included in a box model, AMCOTS (Atmospheric Mercury Chemistry Over The Sea, Hedgecock and Pirrone, 2004)) of multiphase MBL photochemistry along with previously

known Hg gas and aqueous phase chemistry (Pleijel and Munthe, 1995, Lin and Pekhonen, 1999). The AMCOTS results can be compared directly to results from measurement campaigns, (Hedgecock et al., 2003, Hedgecock and Pirrone, 2004). The high measured concentrations of RGM coupled with the modelling support have meant that the cycle of Hg in the MBL, its emission, transport, chemistry and deposition have had to be reconsidered, and the role of the ocean-atmosphere in the global Hg cycle and the global Hg budget reassessed (Mason and Sheu, 2002).

The MBL chemistry of Hg therefore cannot be removed from the transport and physical processes which ultimately have an influence on the concentrations of Hg species in the MBL. Where Hg in the MBL comes from, and which chemical species are emitted or transported with it, can directly or indirectly affect Hg chemistry. The scavenging of Hg compounds by deliquesced aerosol particles or rain droplets, and the dry deposition of oxidised Hg compounds not only exert a major influence over the concentrations of Hg species in the MBL but also on the marine emission/deposition budget. The chemistry of Hg is however not only the central theme of this chapter, but also the central process which links emissions to deposition, governs the lifetime of $Hg^0_{(g)}$ in the MBL, and therefore the influence that marine emissions may have on the global Hg budget.

THE CHEMISTRY OF Hg IN THE MBL

The Gas Phase

One of gas phase elemental mercury's defining characteristics under typical atmospheric conditions of temperature and pressure, and in the presence of typical concentrations of the common tropospheric oxidants, is its general lack of reactivity. $Hg^0_{(g)}$ reacts extremely slowly with O_3, H_2O_2, HCl, and Cl_2, the rates range from 3×10^{-20} to 2.6×10^{-18} $cm^3 molecules^{-1}s^{-1}$ (see table 1). These gases are present at trace concentrations in the parts per billion (ppb = nmol mol^{-1}) to parts per trillion (ppt = pmol mol^{-1}) range. Recently however it has been found that $Hg^0_{(g)}$ reacts much faster with certain radicals present in the troposphere, notably OH, Br and Cl, the concentrations of which are generally very low indeed, so low in fact that direct measurement is very difficult in the field. The concentrations of these radicals are inferred to range from effectively zero to 10^6 - 10^7 molecules cm^{-3}; at 25°C and 1 atmosphere there are in total roughly 2.5×10^{19} molecules cm^{-3}. These maximum radical concentrations, because of their photolytic production mechanisms, occur with maximum incident solar radiation, and

their average concentrations are therefore far lower. The reaction between $Hg^0_{(g)}$ and NO_3 has also been measured (Sommar et al., 1997) but only an upper limit ($k = 4 \times 10^{-15}$ $cm^3 molecule^{-1} s^{-1}$) was reported. NO_3 is a night time oxidant and given the experimental evidence which shows a daytime $Hg^{II}_{(g)}$ maximum it seems unlikely that his reaction plays an important role in the MBL. The reactions with OH, Br and Cl radicals are nonetheless important in Hg cycling because even though their concentrations are low, the relative rapidity with which they oxidise $Hg^0_{(g)}$ compared to other more abundant atmospheric oxidants, mean that these reactions account for the major part of the tropospheric oxidation of $Hg^0_{(g)}$ where they are present. The halogen radicals are found in greater than average abundance during the polar springtime 'Bromine explosion', and also, but to a lesser extent in the MBL and above salt lakes. The OH radical on the other hand is generally more abundant where O_3 concentrations are high, as it is produced mainly by the reaction between water vapour and the O (^{1}D) atom produced by one of the photolysis pathways of O_3. The measurement of the rates of reaction between $Hg^0_{(g)}$ and radical species has only begun recently, and it is only right to point out that not all the measured reaction rates have been independently confirmed, and that there is not unanimous agreement over the results obtained. Comparison between modelling studies and field campaign measurements have in some cases provided some corroboration using the measured reaction rates, but in others have called into question the accuracy of some of the rate constants.

The Aqueous Phase

The atmospheric aqueous phase, cloud and fog droplets and deliquescent aerosol particles play an extremely important role in Hg chemistry and not just in the MBL. As mentioned in the introduction $Hg^{II}_{(g)}$ is much more soluble and less volatile than $Hg^0_{(g)}$, therefore most deposited Hg is Hg^{II}, and wet deposition is often the major Hg deposition process. $Hg^{II}_{(g)}$ is rapidly scavenged in the presence of an atmospheric aqueous phase, $Hg^0_{(g)}$ is also scavenged to a certain extent and both oxidation and reduction processes occur in the aqueous phase. In the absence of the radicals which oxidise Hg in the gas phase, Hg oxidation proceeds much more rapidly in the aqueous phase than the gas phase, predominantly via the reaction with $HOCl_{(aq)}/OCl^-_{(aq)}$ and $O_{3(aq)}$, see Table 1. There is some debate whether oxidised Hg compounds can be reduced in environmental aqueous systems by reaction with $HO_{2(aq)}/O_2^-_{(aq)}$; Pehkonen and Lin (1997) sustained that reduction occurred with a rate constant of 1.1×10^4 $M^{-1} s^{-1}$, while Gårdfeldt, and Jonsson (2003) suggest that the reaction does not proceed under environmental

conditions. The influence of the inclusion or not of this reduction pathway on modelled Hg concentrations in rain has been studied by Bullock (2005) (see Chapter-14). The thermal decomposition of $HgSO_3$ also yields elemental Hg (Table 1). Apart from the redox chemistry which occurs in the aqueous phase, the ionic composition of the droplets or aerosols make a difference to the quantity of $Hg^{II}_{(aq)}$ which can feasibly be associated with the particles. Modelling studies showed that because of the greater number of potential complexes between $Hg^{++}_{(aq)}$ and $Cl^-_{(aq)}$ (and other halides) compared to $OH^-_{(aq)}$ or $SO_3^{2-}_{(aq)}$, that is: $HgCl^+_{(aq)}$, $HgCl_{2(aq)}$, $HgCl_3^-_{(aq)}$ and $HgCl_4^{2-}_{(aq)}$, that higher $Hg^{II}_{(aq)}$ concentrations, by a factor of 100, could be found in droplets with high halide ion concentrations (Forlano et al., 2000). Although this is not generally important in fog and cloud droplets it is potentially very important for sea salt aerosol particles.

The high halide ion concentration found in sea salt particles potentially also has an effect on the speciation of $Hg^{II}_{(g)}$ found in the MBL. HgO has a very high Henry's Law constant and HgO produced by the gas phase oxidation of $Hg^0_{(g)}$ by $OH_{(g)}$ or $O_{3(g)}$, (if it is HgO produced in the reaction, product studies are difficult with $Hg^{II}_{(g)}$ species because they tend to condense on to any available surface), would be rapidly scavenged by the sea salt particles. It would then react with $H^+_{(aq)}$ to give $Hg^{++}_{(aq)}$ which would be complexed as discussed above. Modelling studies show that as the Hg chloride complex concentrations increase the imbalance between the aqueous and gas phase concentrations of $HgCl_2$ results in net outgassing of $HgCl_2$ from the particles.

Mass Transfer

Mass transfer of any species between droplets or deliquesced aerosol particles depends on the Henry's Law constant, the temperature, the droplet radius, the accommodation coefficient of the species involved and the liquid water content (LWC) of the atmosphere. For $Hg^{II}_{(g)}$ species the general direction of the transfer, because of high their Henry's Law constants, is from the gas phase to the aqueous phase. This is certainly the case when the LWC is high, such as in fogs or clouds. However, as described above when the only liquid water is deliquesced aerosol particles, and they high concentrations of halide ions (sea salt aerosol can have $Cl^-_{(aq)}$ concentrations over 5M) it is possible that Hg^{II} species such as $HgCl_2$ pass from the aqueous to the gas phase. $Hg^0_{(g)}$ however is relatively insoluble and has a low Henry's Law constant, see Table 1, and its aqueous phase concentration is low. The equilibrium concentration in the aqueous phase is determined by the Henry's Law constant, the rate at which equilibrium is reached, however, depends on

Table 1. The Hg chemistry included in AMCOTS.

Mercury Reactions and Equilibria	k or K (298K)	Reference
$Hg^0_{(g)} + O_{3(g)} \to HgO_{(g)}$	3.0×10^{-20} cm^3 molec^{-1} s^{-1}	(a)
$Hg^0_{(g)} + O_{3(g)} \to HgO_{(g)}$	7.5×10^{-19} cm^3 molec^{-1} s^{-1}	(b)
$Hg^0_{(g)} + H_2O_{2(g)} \to HgO_{(g)}$	8.5×10^{-19} cm^3 molec^{-1} s^{-1}	(c)
$Hg^0_{(g)} + OH_{(g)} \to HgO_{(g)}$	8.7×10^{-14} cm^3 molec^{-1} s^{-1}	(d)
$Hg^0_{(g)} + HCl_{(g)} \to \to HgCl_{2(g)}$	1×10^{-19} cm^3 molec^{-1} s^{-1}	(e)
$Hg^0_{(g)} + Cl_{2(g)} \to HgCl_{2(g)}$	2.6×10^{-18} cm^3 molec^{-1} s^{-1}	(f)
$Hg^0_{(g)} + Cl_{(g)} \to \to HgCl_{2(g)}$	1×10^{-11} cm^3 molec^{-1} s^{-1}	(f)
$Hg^0_{(g)} + Br_{2(g)} \to HgBr_{2(g)}$	9×10^{-17} cm^3 molec^{-1} s^{-1}	(f)
$Hg^0_{(g)} + Br_{(g)} \to \to HgBr_{2(g)}$	3.2×10^{-12} cm^3 molec^{-1} s^{-1}	(f)
$Hg^0_{(aq)} + O_{3(aq)} \to HgO_{(aq)}$	4.7×10^7 M^{-1} s^{-1}	(g)
$HgO_{(aq)} + H^+_{(aq)} \to Hg^{++}_{(aq)} + OH^-_{(aq)}$	1×10^{10} M^{-1} s^{-1}	(h)
$Hg^{++}_{(aq)} + OH^-_{(aq)} \to HgOH^+_{(aq)}$	3.9×10^{10} M^{-1}	(h)
$HgOH^+_{(aq)} + OH^-_{(aq)} \to Hg(OH)_{2(aq)}$	1.6×10^{11} M^{-1}	(h)
$HgOH^+_{(aq)} + Cl^-_{(aq)} \to HgOHCl_{(aq)}$	2.7×10^7 M^{-1}	(h)
$Hg^{++}_{(aq)} + Cl^-_{(aq)} \to HgCl^+_{(aq)}$	5.8×10^6 M^{-1}	(h)
$HgCl^+_{(aq)} + Cl^-_{(aq)} \to HgCl_{2(aq)}$	2.5×10^6 M^{-1}	(h)
$HgCl_{2(aq)} + Cl^-_{(aq)} \to HgCl_3^-_{(aq)}$	6.7 M^{-1}	(i)
$HgCl_3^-_{(aq)} + Cl^-_{(aq)} \to HgCl_4^{--}_{(aq)}$	13 M^{-1}	(i)
$Hg^{++}_{(aq)} + Br^-_{(aq)} \to HgBr^+_{(aq)}$	1.1×10^9 M^{-1}	(i)
$HgBr^+_{(aq)} + Br^-_{(aq)} \to HgBr_{2(aq)}$	2.5×10^8 M^{-1}	(i)
$HgBr_{2(aq)} + Br^-_{(aq)} \to HgBr_3^-_{(aq)}$	1.5×10^2 M^{-1}	(i)
$HgBr_3^-_{(aq)} + Br^-_{(aq)} \to HgBr_4^{--}_{(aq)}$	23 M^{-1}	(i)
$Hg^{++}_{(aq)} + SO_3^{--}_{(aq)} \to HgSO_{3(aq)}$	2.1×10^{13} M^{-1}	(j)
$HgSO_{3(aq)} + SO_3^{--}_{(aq)} \to Hg(SO_3)_2^{--}_{(aq)}$	1.0×10^{10} M^{-1}	(j)
$HgSO_{3(aq)} \to Hg^0_{(aq)} +$ products	0.0106 s^{-1}	(k)
$Hg^0_{(aq)} + OH_{(aq)} \to Hg^+_{(aq)} + OH^-_{(aq)}$	2.0×10^9 M^{-1} s^{-1}	(l)
$Hg^+_{(aq)} + OH_{(aq)} \to Hg^{++}_{(aq)} + OH^-_{(aq)}$	1.0×10^{10} M^{-1} s^{-1}	(l)
$Hg^{II}_{(aq)} + O_{2\ (aq)} \to Hg^+_{(aq)} + O_{2(aq)}$	1.1×10^4 M^{-1} s^{-1}	(m)
$Hg^{II}_{(aq)} + HO_{2(aq)} \to Hg^+_{(aq)} + O_{2(aq)} + H^+_{(aq)}$	1.1×10^4 M^{-1} s^{-1}	(m)
$Hg^+_{(aq)} + O_2^-_{(aq)} \to Hg_{(aq)} + O_{2(aq)}$	fast	(m)
$Hg^+_{(aq)} + HO_{2(aq)} \to Hg^0_{(aq)} + O_{2(aq)} + H^+_{(aq)}$	fast	(m)
$Hg^{II}_{(aq)} + O_2^-_{(aq)} \to Hg^+_{(aq)} + O_{2(aq)}$	0	(n)
$Hg^{II}_{(aq)} + HO_{2(aq)} \to Hg^+_{(aq)} + O_{2(aq)} + H^+_{(aq)}$	0	(n)
$Hg_{(aq)} + HOCl_{(aq)} \to Hg^{++}_{(aq)} + Cl^-_{(aq)} + OH^-_{(aq)}$	2.09×10^6 M^{-1} s^{-1}	(o)
$Hg_{(aq)} + ClO^-_{(aq)} \to Hg^{++}_{(aq)} + Cl^-_{(aq)} + OH^-_{(aq)}$	1.99×10^6 M^{-1} s^{-1}	(o)
$Hg^0_{(g)} \leftrightarrow Hg^0_{(aq)}$	0.13 M atm^{-1}	(p)
$HgO_{(g)} \leftrightarrow HgO_{(aq)}$	2.69×10^{12} M atm^{-1}	(p)
$HgCl_{2(g)} \leftrightarrow HgCl_{2(aq)}$	2.75×10^6 M atm^{-1}	(p)
$HgBr_{2(g)} \leftrightarrow HgBr_{2(aq)}$	2.75×10^6 M atm^{-1}	(q)
$HgO_{(g)} \to$ deposition	2.0 cm s^{-1}	(r)
$HgCl_{2(g)} \to$ deposition	2.0 cm s^{-1}	(r)
$HgBr_{2(g)} \to$ deposition	2.0 cm s^{-1}	(q)

(a) Hall (1995), (b) Pal and Ariya (2004), (c) Tokos et al. (1998), (d) Sommar ct al., (2001), (e) Hall and Bloom (1993), (f) Ariya et al. (2002), (g) Munthe (1992), (h) Pleijel and Munthe (1995), (i) Clever et al. (1985), Van Loon et al. (2001), (k) Van Loon et al. (2000), (l) Lin and Pehkonen (1997), (m) Pehkonen and Lin (1997), (n) Gårdfeldt, and Jonsson (2003), (o) Lin and Pehkonen (1999), (p) Schroeder and Munthe (1998), (q) Hedgecock and Pirrone, 2004, (r) Hedgecock and Pirronc, 2001.

a number of factors as shown below. The rate of change of the aqueous phase concentration is given in equation 1, following the notation of Sander (1999),

$$dc_a/dt = k_{mt} (c_{g,\infty} - c_{a,surf} / k_H RT) \tag{1}$$

where c_a is the aqueous phase concentration of the species (mol m^{-3}$_{aq}$),

$c_{a,surf}$ the aqueous phase concentration at the surface (mol m^{-3}$_{aq}$), $c_{g,\infty}$ the background gas phase concentration (mol m^{-3}$_{air}$), k_H the Henry's Law constant (mol m^{-3}$_{aq}$ Pa^{-1}), R the gas constant (J mol^{-1} K^{-1}) and T the temperature (K). k_{mt} is the mass transfer coefficient, defined as:

$$k_{mt} = (r^2/3D_g + 4r/3\alpha v)^{-1} \tag{2}$$

where r is the droplet radius (m), D_g the gas phase diffusivity (m^{2}s^{-1}), v the mean molecular velocity (ms^{-1}) and α the accommodation coefficient (dimensionless). k_{mt} is expressed in s^{-1}, but contains the conversion m^3$_{air}$ to m^3$_{aq}$, Sander (1999).
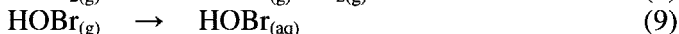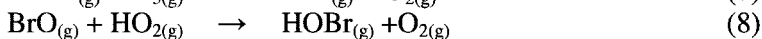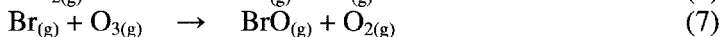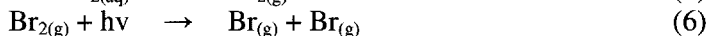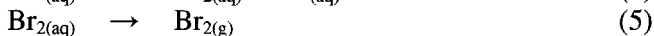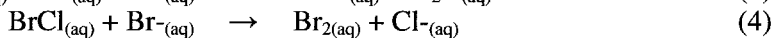
As can be seen from equation 2, the mass transfer coefficient is inversely proportional to the square of the droplet radius, hence the very small aerosol droplets reach aqueous phase equilibrium rapidly. Larger droplets such as cloud or rain droplets take significantly longer. Some droplets may not reach equilibrium during the lifetime of a cloud or if they are precipitating, thus chemical models tend to model mass transfer as a kinetic rather than equilibrium process.

General MBL Photochemistry

Mass transfer between phases turns out to be very important in MBL photochemistry in general. The chemistry of the MBL is distinguished from other parts of the atmosphere by its constantly high relatively humidity, usually above the deliquescence point of sea salt and non-sea-salt (nss) sulphate aerosols, and almost always higher than the crystallization point, this means that aerosol emitted from the sea surface as liquid droplets remain liquid and do not crystallize. The sea-salt aerosol droplets are characterised by high concentrations of Cl$^-$ and Br$^-$ ions; the acidification of freshly produced sea salt aerosol, which is slightly alkaline, triggers a series of chemical responses in the aerosol, such as the acid displacement of HCl and the production of neutral, relatively insoluble Br containing species in the

aqueous phase which then pass from the aqueous to the gas phase according to their Henry's Law constant.

The release of halogen containing species from aerosol particles is the key to the difference between Hg chemistry in the MBL and elsewhere in the troposphere. The conversion of bromide ions present in sea salt particles to less soluble and volatile Br containing species, particularly Br_2 and BrCl, which degas from the aerosol, is initiated by its reaction with $O_{3(aq)}$, $OH_{(aq)}$, $NO_{3(aq)}$, $N_2O_{5(g)}$ or $HSO_5^-{}_{(aq)}$, (Sander et al., 2003; von Glasow et al., 2002). Vogt et al., 1996 proposed an autocatalytic cycle starting from the reaction of HOBr with Cl⁻ in the presence of acid as shown below (from Sander et al., 2003);

$$HOBr_{(aq)} + Cl^-{}_{(aq)} + H^+{}_{(aq)} \rightarrow BrCl_{(aq)} + H_2O_{(aq)} \tag{3}$$

$$BrCl_{(aq)} + Br^-{}_{(aq)} \rightarrow Br_{2(aq)} + Cl^-{}_{(aq)} \tag{4}$$

$$Br_{2(aq)} \rightarrow Br_{2(g)} \tag{5}$$

$$Br_{2(g)} + h\nu \rightarrow Br_{(g)} + Br_{(g)} \tag{6}$$

$$Br_{(g)} + O_{3(g)} \rightarrow BrO_{(g)} + O_{2(g)} \tag{7}$$

$$BrO_{(g)} + HO_{2(g)} \rightarrow HOBr_{(g)} + O_{2(g)} \tag{8}$$

$$HOBr_{(g)} \rightarrow HOBr_{(aq)} \tag{9}$$

which leads to the net reaction;

$$Br^-{}_{(aq)} + H^+{}_{(aq)} + O_{3(g)} + HO_{2(g)} + h\nu \rightarrow Br_{(g)} + 2O_{2(g)} + H_2O_{(aq)} \tag{10}$$
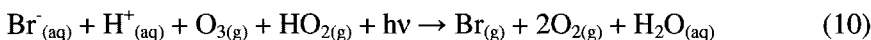
or alternatively expressed, see von Glasow et al. (2002);

$$2HO_{2(g)} + H^+{}_{(aq)} + 2O_{3(g)} + Br^-{}_{(aq)} + h\nu \rightarrow HOBr_{(g)} + 4O_{2(g)} + H_2O_{(aq)} \tag{11}$$
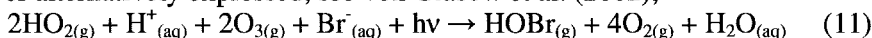
It is the release of Br containing compounds which is of most interest for Hg chemistry. The difference in the release mechanisms of Br and Cl from the sea salt aerosol results in Cl being released to a large extent as HCl, whilst Br is emitted mostly as Br_2 or BrCl. HCl is stable chemically and photolytically, whereas Br_2 and BrCl are rapidly photolysed to their atomic constituents. The gas phase concentration of reactive Br compounds is therefore higher than the concentration of reactive Cl compounds, with the result that the Br compounds have more influence on Hg chemistry than Cl compounds, even thought the reaction with the Cl atom is the fastest of the known reactions between $Hg^0{}_{(g)}$ and the halogen atoms and compounds (Arya et al., 2002).

Modelling MBL Chemistry

A number of box and 1-dimensional modelling studies of MBL chemistry have been published in recent years, most of which concentrate on the role of

the marine aerosol in the production of reactive halogen compounds (Sander and Crutzen,1996, Vogt et al., 1996; Toyota et al., 2001; von Glasow et al., 2002; Toyota et al., 2003). These models have increased in complexity and now take into account both sea salt and non-sea-salt sulphate particles, some including particle size distributions, and sea salt aerosol production. The chemistry in these models focuses on halogen gas and aqueous phase chemistry but also include NO_x, HO_x and SO_x chemistry. Non-methane hydrocarbons are included in all the models with varying levels of detail. The most complex treatment is given in Toyota et al. (2003). The AMCOTS model uses the reaction database from von Glasow et al. (2002) which includes CH_4, C_2H_6, C_2H_4, and their reaction products in the gas phase and where the products are soluble, the aqueous phase.

The rate and extent of halogen release from sea salt aerosols under varying atmospheric conditions is discussed in more detail below, but in terms of Hg chemistry; for more general information the reader is referred to von Glasow et al. (2002), Sander et al. (2003), Toyota et al. (2003), and references therein.

FACTORS INFLUENCING THE RATE OF $Hg^0_{(g)}$ OXIDATION IN THE MBL

Br production

In clean MBL air, with low levels of NO_x and O_3, the concentration of OH is low and the major $Hg^0_{(g)}$ oxidant species will be $Br_{(g)}$. Therefore the factors which influence $Br_{(g)}$ concentrations will have a direct effect on the rate at which $Hg^0_{(g)}$ is oxidised and thus the concentration of $Hg^{II}_{(g)}$. Among the more important factors influencing the rate and extent of halogen activation in the MBL are the wind speed, the temperature, the intensity of solar radiation and latitude.

Wind speed, which determines the production of sea salt aerosol particles, has a direct effect on atmospheric sea salt LWC. Increasing sea salt LWC increases the scavenging rate of $Hg^{II}_{(g)}$ and can therefore lower the gas phase concentration. However, increased sea salt LWC also potentially supplies more $Br_{(g)}$ to the MBL increasing its capacity to oxidise $Hg^0_{(g)}$, but increases in the aerosol numbers, and/or size, increase the buffering capacity of the MBL because freshly produced sea salt aerosol is alkaline, and therefore the acid dependent halogen activation mechanism takes longer to start. A theoretical box model study of the lifetime of $Hg^0_{(g)}$ in the MBL showed that up to a threefold increase in sea salt LWC (from 3×10^{-11} to 9×10^{-11} m^3_{aq}/m^3_{air}) increased the rate of $Hg^0_{(g)}$ oxidation, whereas decreasing the sea

salt LWC decreased the rate (Hedgecock and Pirrone, 2004). One of the problems with a box model study is that a constant aerosol loading is assumed to the top of the model volume, which is not the case given that production occurs at the surface. Both model and experimental studies need to confront this aspect of MBL chemistry.

From the net equations describing Br release from the sea salt aerosol above, it can be seen that acid is consumed, and therefore the originally alkaline sea salt particles need to take up acidic gases from the atmosphere to initiate the process. The air temperature influences the solubility of gases, thus lower temperatures favour the more rapid uptake of acidic gases, accelerating the rate of acidification of the sea salt particles and halogen activation (von Glasow et al., 2002).

The intensity of solar irradiation is important both for the photolysis of Br containing compounds, but also for the production of $HO_{2(g)}$ which is the major sink for $BrO_{(g)}$ in the MBL. Because the oxidation of $Hg^0_{(g)}$ depends on photolytically produced oxidants the rate naturally depends on both latitude and time of year, Figures 1a and b, (Hedgecock and Pirrone, 2004).

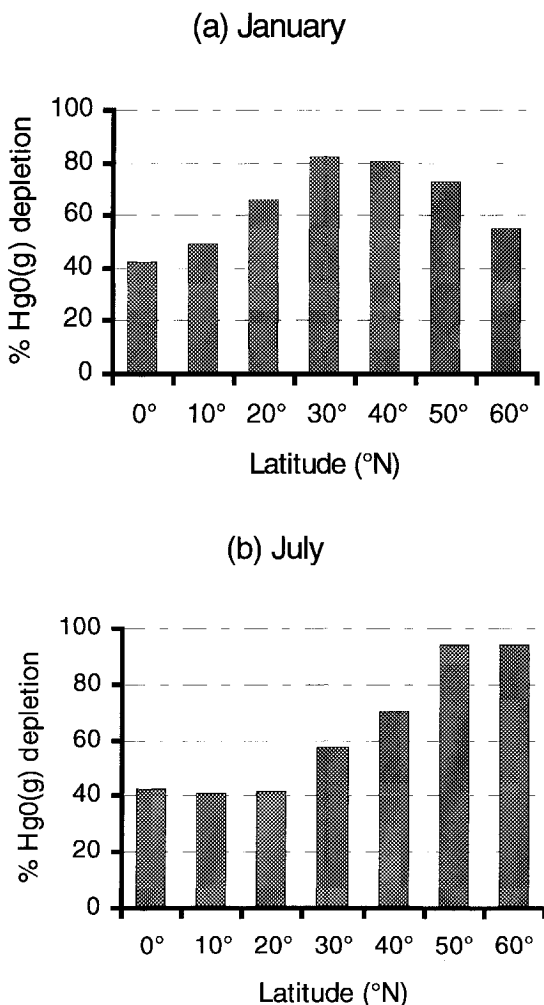Hedgecock and Pirrone (2004) also showed that some cloud cover could

(a) January

(b) July

Figure 1. The modelled percentage depletion of $Hg^0_{(g)}$ after 1 week as a function of latitude for the months of January and July.

actually enhance the rate at which $Hg^0_{(g)}$ is oxidised in the MBL. Figure 2 shows an example of this phenomenon, the $Hg^0_{(g)}$ depletion was modelled for January at a latitude of 10° N, and it can be clearly seen that increasing the cloud cover up to an optical depth of 20 increases $Hg^0_{(g)}$ depletion with respect to the clear sky simulations.

The reason for this is that the attenuation of the incoming solar radiation produced by clouds is not equal over the UV-visible spectrum, it is more marked at shorter than at longer wavelengths. Br_2 and BrCl photolysis begins earlier in the morning and ceases later in the evening than O_3 photolysis because the solar spectrum in the lower troposphere is shifted to the red at high solar zenith angles.

This accounts for the earlier build-up of $Br_{(g)}$ in the MBL, because in the early morning the longer path which sunlight travels through the atmosphere means that Br_2 photolysis commences earlier. In fact the Br produced reacts with O_3 to produce BrO, a phenomenon called 'sunrise ozone destruction', (Nagao et al., 1999). The concentration of BrO in fact peaks at dawn

(a) January 30° N

(b) July 30° N

Figure 2. The influence of cloud optical depth on $Hg^0_{(g)}$ depletion at 10 ° N during January, after one week of model simulation.

and dusk, it has a minimum around midday when $HO_{2(g)}$ concentrations are at their maximum (von Glasow et al., 2002).

This increase in $Hg^0_{(g)}$ oxidation rate occurs only at certain latitudes and at certain times of the year, and only up to a certain cloud optical depth, after which the rate of oxidation decreases.
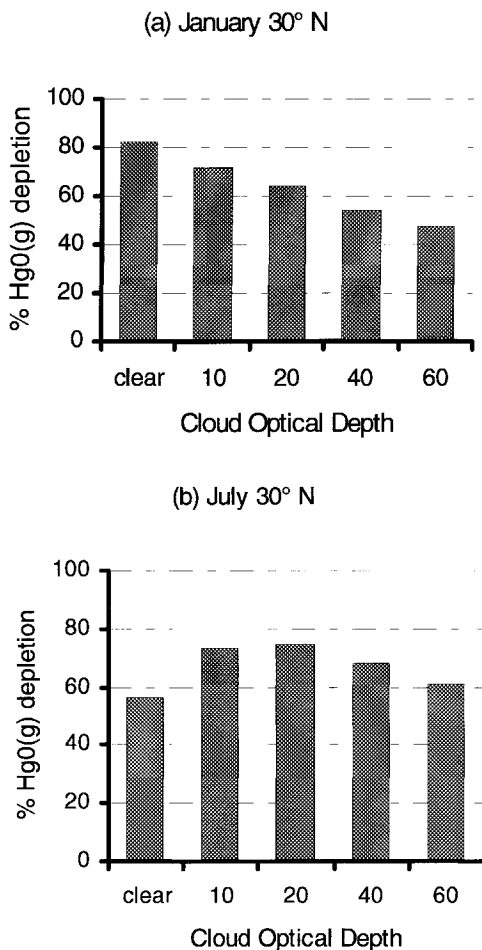
OH production

As well as $Br_{(g)}$, $OH_{(g)}$ is potentially a major contributor to the production of $Hg^{II}_{(g)}$ in the MBL. In the clean MBL it is likely to be significantly less important than $Br_{(g)}$ due to the low O_3 concentrations found and the low concentrations of possible O_3 precursors such as NO_x. However, in regions where the MBL is influenced by continental air masses which contain urban or industrial NO_x emissions, it is possible that conditions are amenable to $OH_{(g)}$ production. Such conditions would also result in higher $HO_{2(g)}$ concentrations than in the clean MBL, thus suppressing $BrO_{(g)}$, which, because BrO photolysis is the main source of $Br_{(g)}$, reduces the role of $Br_{(g)}$ at the same time.

A prime example of a region where the MBL is directly affected by continental emissions is the Mediterranean Sea. A combination of meteorological factors, boundary layer air flow is slow but generally from north to south, high levels of solar irradiation, stable anticyclonic conditions and little rain, provide all the ingredients in the Mediterranean summer for O_3 production. Concentrations of O_3 at ground level across the whole Mediterranean regularly exceed the European 8 hour exposure limit (Nolle et al., 2002; Lelieveld et al., 2002). It is probable that the contribution of $OH_{(g)}$ to the MBL oxidation of $Hg^0_{(g)}$ under such conditions is greater than that of $Br_{(g)}$, partly because of the higher $OH_{(g)}$ concentration and partly because of the effect that higher $HO_{2(g)}$ concentrations would have on the production of $Br_{(g)}$ as described above. This hypothesis is supported by recent modelling studies as described below.

$Hg^{II}_{(g)}$ IN THE MBL: MODELLING vs. MEASUREMENTS

The first measurements of RGM in the MBL (rather than at coastal sites) were made during three cruises between 1999 and 2000 near to the Bermuda Time Series Station (BATS; 31.678N, 64.178W), in the North Atlantic, (Mason et al, 2001), using the filter pack technique (Sheu and Mason, 2001) and in the Mediterranean in 2000 (Sprovieri et al., 2003), using the annular denuder technique (Landis et al., 2002). Since then there have been further measurement campaigns in the North Pacific in 2002 (Laurier et al., 2003), and in the Mediterranean in 2003 and 2004 (F. Sprovieri, private communication), during these cruises $Hg^0_{(g)}$ and $Hg^{II}_{(g)}$ were measured using the same techniques and the same type of instrument: the Tekran 1130 speciation unit coupled with to the Tekran 2537A analyser (Tekran Inc.,

Toronto, Canada). The time resolution of the measurements was two or four hours.

The first attempt to model MBL $Hg^{II}_{(g)}$ concentrations used measured $Hg^0_{(g)}$ concentrations and ancillary data obtained during from the first Mediterranean cruise campaign in 2000 as input and using a box model of MBL photochemistry with Hg chemistry included, sought to reproduce the measured $Hg^{II}_{(g)}$ concentrations. The box model itself is described in Hedgecock and Pirrone (2001), and the results of the comparison between modelled and measured $Hg^{II}_{(g)}$ concentrations in Hedgecock et al. (2003).

That original model did not include the reaction of $Hg^0_{(g)}$ with $Br_{(g)}$, as the rate constant was determined after the modelling studies were performed and the model unsurprisingly underestimated somewhat the $Hg^{II}_{(g)}$ concentrations, although the minima and the diurnal variation in $Hg^{II}_{(g)}$ was reproduced reasonably well.
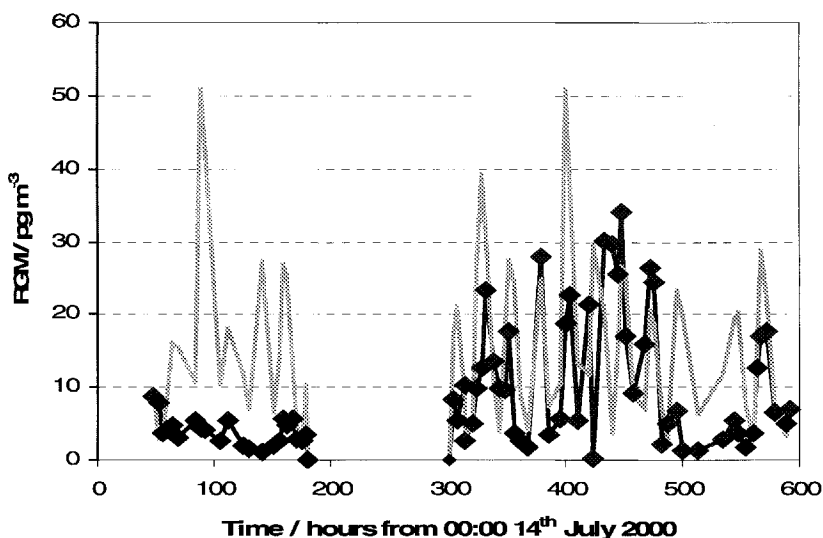
Figure 3. Measured (dark line with diamonds) and modelled with $z_{(surface\ mixed\ layer)}$ set at 300m (light line) RGM values (pg m-3) from the Mediterranean campaign.

Later studies included the $Hg^0_{(g)} + Br_{(g)}$ reaction and, in order to simulate halogen activation more accurately, both the sea salt and non-sea-salt sulphate aerosols were included (Hedgecock and Pirrone, 2004); the previous model included only the sea salt aerosol.

This latest version of the box model, AMCOTS, (Atmospheric Mercury Chemistry Over The Sea) is being used (work in progress) to re-analyse the

data from the Mediterranean campaign aboard the R.V. Urania in 2000, and the north Pacific campaign aboard the R.V. Melville in 2002. This new version of the model uses the measured $Hg^0_{(g)}$ concentrations and ancillary chemical and meteorological data, to model the $Hg^{II}_{(g)}$ concentration, similarly to Hedgecock et al. (2003). Some preliminary results for the Mediterranean are shown in Figure 3.

Two things need to be mentioned regarding the application of a box model to measured data, the first is that precipitation and sea surface conditions, are not taken into account. Both increased sea salt aerosol and precipitation increase the rate at which $Hg^{II}_{(g)}$ is scavenged, due to the increased atmospheric liquid water content. The first period of the oceanographic campaign was characterised by rough seas and rain, which accounts for the model's overestimation of the $Hg^{II}_{(g)}$ concentration (Figure 3). The second, is that a box model requires that the box height is included as input in order to calculate the rate of dry deposition and emission to and from the sea surface. Typical values of the MBL height (z_{MBL}) are 1000m for the remote MBL (such as the Pacific, Sander et al., 1996) and 400m for the summertime Mediterranean (Kallos et al., 1998) respectively. However the height of the capping inversion over the MBL does not always correspond to the height of the surface mixed layer, (Garratt, 1992), and in a model of MBL aerosol formation from biogenic iodine emissions, O'Dowd et al. (2002) used a globally averaged value of 300m for the height of the surface mixed layer. The mixed layer height also varies near the coast when advection of air across the coastline results in a thermal internal boundary layer (Garratt, 1992). The height of the boundary layer over the Mediterranean Sea is relatively stable but variations between day and night do occur. The actual height of the surface mixed layer is not simple to determine, (Seibert et al., 2000), and in the absence of appropriate measurements meteorological models which calculate advection and transport could be one means of providing an estimate from the surface mixed layer height. Unfortunately complex chemical models such as AMCOTS with over 200 chemical species and 900 reactions are too computationally expensive to be linked directly to meteorological / dispersion models to perform regional simulations over the periods of measurement campaigns. However, models such as the Regional Atmospheric Modelling System (RAMS) (ATMET, 2004) can be used to estimate the height of the mixing layer, using variation in Turbulent Kinetic Energy (TKE), the virtual potential temperature (θ_v) or the relative humidity. Simulations using nested grids for the period and area of the last half of the Urania cruise suggest that the mixing layer height varied between less than 150m to around 350m.

Figure 4 shows the results assuming that the mixing layer height ($z_{surface\ mixed\ layer}$) varies as indicated by the RAMS TKE values for the second period

of the Mediterranean campaign in 2000. The model output is averaged over four hours to correspond to the sampling time used in the measurements.

One of the main reasons for attempting to model measured $Hg^{II}_{(g)}$ is partly to see if known Hg chemistry is comprehensive enough to make sense of the observations. In fact the first modelling studies (Hedgecock and Pirrone, 2001; Hedgecock et al., 2003) $Hg^{II}_{(g)}$ concentrations were underestimated.

Modelling studies also help to identify the predominant oxidation pathways, because the model uses measured data to recreate the chemistry, allowing reaction rates to be followed individually during the simulation. This last approach has recently identified what appears to be a difference between open ocean and closed sea oxidation of $Hg^{0}_{(g)}$. Preliminary simulations for the Pacific data (Laurier et al, 2003) and Mediterranean data (Sprovieri et al, 2003) indicate that although Br was the most important oxidant in the Pacific whilst in the Mediterranean most oxidation was the result of the reaction with $OH_{(g)}$. This is most likely to be due to the higher $O_{3(g)}$ concentrations and temperatures in the Mediterranean, however it is too soon to draw hard and fast conclusions.
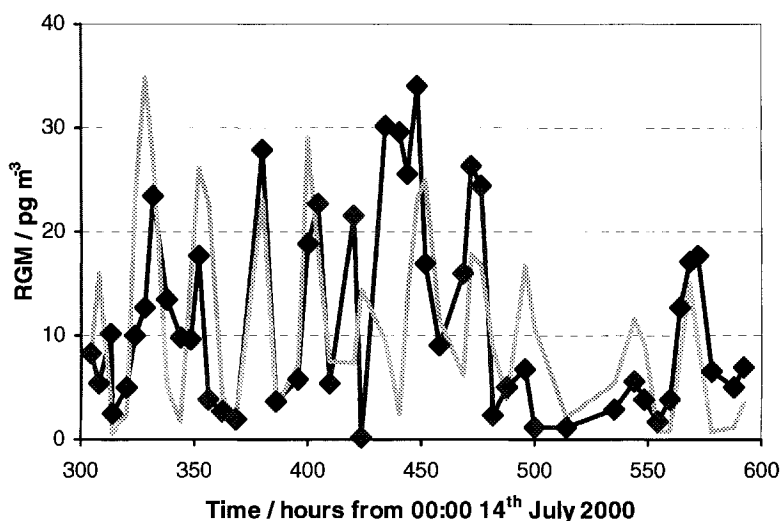

Figure 4. Measured (dark line with diamonds) and modelled (light line) RGM values (pg m^{-3}) from the Mediterranean campaign, with z$_{(surface\ mixed\ layer)}$ temporal variation calculated using RAMS.

IMPLICATIONS OF Hg CHEMISTRY IN THE MBL

The relatively new discovery of $Hg^{II}_{(g)}$ formation in the MBL is changing some of the assumptions previously made about atmospheric Hg, its cycling between air and sea, its emission from the world's oceans and the global Hg budget. A few of the more important of these are briefly described here, a fuller discussion may be found in the relevant chapters of this book and the literature cited below.

The lifetime of $Hg^0_{(g)}$ in the MBL

The AMCOTS model has been used to estimate the atmospheric lifetime of $Hg^0_{(g)}$ in the MBL, (Hedgecock and Pirrone, 2004). Using the approach of Seinfield and Pandis, (1998) the atmospheric lifetime (τ) of $Hg^0_{(g)}$ is the sum of the inverse of the oxidation reaction rates (rate constant multiplied by concentration :

$$\tau = \{k(Hg^0+O_3).[O_3] + k(Hg^0+OH).[OH] + k(Hg^0+Br).[Br]\}^{-1} \text{ s} \qquad (12)$$

thus

$$\tau^{-1} = 3\times10^{-20} [O_3] + 8.7\times10^{-14} [OH] + 3.2\times10^{-12} [Br] \text{ s}^{-1} \qquad (13)$$

from AMCOTS, the modelled one week average concentrations of the oxidants found using average cloud optical depths for summer, at 10, 40 and 60° N were 21 ppb O_3, OH in the range $5\text{-}20\times10^5$ molecules cm^{-3}, and Br around 3×10^5 molecules cm^{-3},

$$\tau^{-1} = 2\times10^{-8} + 8.7\times10^{-8} + 1\times10^{-6}$$
thus, $\tau = 10.5$ days, $\qquad (14)$

alternatively the lifetime with respect to the individual reactions under the model conditions are: $(Hg^0+O_3) = 578$ days, $(Hg^0+OH) = 133$ days and $(Hg^0+Br) = 11.5$ days days. Using the newly measured value for Hg^0+O_3 (Pal and Ariya, 2004) the calculation gives:

$$\tau^{-1} = 7.5\times10^{-19} [O_3] + 8.7\times10^{-14} [OH] + 3.2\times10^{-12} [Br] \text{ s}^{-1} \qquad (15)$$
$$\tau^{-1} = 3.9\times10^{-7} + 8.7\times10^{-8} + 1\times10^{-6} \qquad (16)$$

thus, $\tau = 7.8$ days, $(Hg^0+O_3) = 29$ days, $(Hg^0+OH) = 133$ days and $(Hg^0+Br) = 11.5$ days.

Such a short lifetime for $Hg^0_{(g)}$ is not found in other parts of the atmosphere and has implications for the cycle of Hg in the marine troposphere as discussed below.

Marine emissions of Hg^0 and the global Hg budget

The world's oceans are a source of Hg^0 as well as a receptor for Hg^{II}. The potentially rapid cycling of Hg in the MBL seems to conflict with the well known fact that the hemispherical background concentration of $Hg^0_{(g)}$ is both uniform and constant. The depletion in $Hg^0_{(g)}$ concentrations simulated by Hedgecock and Pirrone (2004) are not seen in the field and imply that the Hg being lost via oxidation and deposition is constantly being replaced. Therefore Hedgecock and Pirrone (2004) included emissions in their model to maintain a stable $Hg^0_{(g)}$ concentration and calculated the emission rates under typical conditions of cloud cover, and temperature for different seasons at different latitudes. The emission rates obtained were of the same order of magnitude as the measured data available in the literature, illustrating that oxidation in the MBL is not incompatible with stable background concentrations. It should also be borne in mind that replenishment of $Hg^0_{(g)}$ in the MBL may be partially due to exchange with the free troposphere as is the case for O_3.

Model improvements required

The next steps in improving MBL Hg chemistry models will include moving to 1 or more dimensional models which allow the variation with height of atmospheric LWC, aerosol pH, and particularly halogen species concentrations. This should serve to avoid the problems of varying surface mixed layer height, and ideally if combined with height resolved measurements of $Hg^0_{(g)}$ and $Hg^{II}_{(g)}$, allow the determination of the relative influences of Hg replenishment from ocean surface emissions and entrainment of Hg from the free troposphere. It will also require that there be some representation of sea salt aerosol production and its advection in the MBL.

Currently AMCOTS uses two mono-disperse distributions to describe the sea salt and sulphate aerosol particles. This is another point where MBL photochemical models have progressed by beginning to use size segregated bins to describe the aerosol population (Toyota et al., 2001, von Glasow et al., 2002), although even this method averages aqueous phase concentrations over size bins, it is nonetheless better than averaging concentrations over the

whole aerosol population. Inclusion of a full description of MBL and Hg chemistry in 3-d meteorological / dispersion models is hindered by the time that the calculations would require. They are also a less appropriate tool for sensitivity studies because the meteorological model input data cannot be changed simply parameter by parameter in the same way that it can with box and 1-d models.

Useful data

There are two specific sets of data which would improve the understanding of MBL Hg chemistry in particular but also Hg chemistry in general. The first is reaction rate data. There is still no real consensus on the rates, or mechanisms, or products of the potentially most important $Hg^0_{(g)}$ oxidation reactions. This is partly because interest in determining these rates is recent, as the number of experimental and theoretical studies published in the last two to three years shows, and partly due to practical difficulties in performing the experiments. It should be mentioned also that $Hg^{II}_{(g)}$ and $Hg^{II}_{(aq)}$ reduction reactions, chemical and photolytic could play an important role in atmospheric Hg chemistry, but few data are available. The aqueous phase photo-reduction of Hg^{II} compounds in particular is important for modelling emissions and to establish the magnitude of sea-air exchange resulting from Hg^{II} deposition and Hg^0 emission. The other type of data which would prove extremely useful is speciated $Hg^{II}_{(g)}$ measurements. At present it is not possible to distinguish HgO, from $HgCl_2$ and $HgBr_2$ using highly time resolved techniques in the field. Should this become practically feasible one of the major obstacles to being certain that atmospheric Hg chemistry is understood would be overcome.

Planning measurement campaigns

The ancillary data obtained during measurement campaigns is of fundamental importance to the interpretation and modelling of Hg compound concentration measurements. The current knowledge of atmospheric Hg chemistry means that without O_3 concentration data, UV-A and UV-B intensities, relative humidity, and temperature, the data pertaining to Hg is almost very difficult to interpret and therefore effectively useless. Measurements of SO_2 and CO as indicators of anthropogenic influence on air masses is also useful. Specific data that would be of particular use in interpreting data from the MBL are the atmospheric LWC and size-resolved aerosol Hg concentrations. If these measurements could be performed at

different altitudes the results would almost certainly be fascinating. The practical complexities involved however are numerous.

CONCLUSIONS

Hg chemistry in the MBL is now rightly a part of the wider research effort to understand the atmospheric cycling of Hg, as it is via the atmosphere that Hg is transported from emission source to receptor site. The deposition and subsequent uptake of Hg by plants and animals can represent a major problem to their well-being, particularly to higher animals, as discussed elsewhere in this book. The transport of $Hg^0_{(g)}$, the overall impact of marine Hg^0 emissions, the deposition of Hg^{II} to open oceans, and perhaps more importantly to coastal areas, are all directly influenced by Hg chemistry in the MBL.

The lifetime of $Hg^0_{(g)}$ in the MBL depends on sea salt aerosol production and loading, and therefore wind speed, on incoming solar radiation thus on latitude, time of year and cloud cover, air temperature and the chemical composition of the MBL. There may therefore be great variability in the lifetime of $Hg^0_{(g)}$, but it can be short which would preclude long range transport, and suggest that a multi-hop mechanism is more likely.

Emissions (or re-emissions) of Hg^0 from the sea contribute to the atmospheric burden of Hg, however oxidation in the MBL and re-deposition could mitigate the effect of these emissions. It should not be forgotten however that the conditions which favour atmospheric oxidation may also favour photo-reduction in marine waters.

The potential impact on coastal environments that the deposition of Hg^{II} resulting from the confluence of more polluted continental air and cleaner but possibly more highly oxidising marine air is an aspect of MBL Hg chemistry which merits further investigation.

The increased understanding of Hg chemistry in the MBL, just as in so many fields of study, increases the number of questions for which an answer may soon be found. In spite of rapid progress many of the conclusions reached with the help of a better understanding of MBL Hg chemistry are still qualitative; clearly the next steps will be towards quantitative answers, particularly regarding deposition / emission in the open ocean, and deposition in coastal areas.

ACKNOWLEDGEMENTS

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