

Mercury cycling in the Environment - Effects of Climate Change

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Summary

Two simple models have been used to evaluate the possible effect of climate change in respect to changed atmospheric oxidation potential of mercury and re-emission from the oceans. In both cases only the effect of temperature increase was considered. This is an obvious limitation considering the complexity of mercury cycling as a whole. However, the result suggests that in a warmer climate gas phase oxidation of GEM in the marine troposphere may be less efficient causing the mercury concentration in the atmosphere to increase. Simultaneously the mercury re-emission flux from the ocean to the atmosphere tends to increase. If this really is the case it means that part of the oceanic mercury pool will be moved to the atmosphere. The environmental effect of that is not obvious. A somewhat higher GEM concentration is not harmful as such, but means that mercury distribution via the atmosphere could be even more important in the future. Another conceivable consequence of mercury being moved from the sea to the atmosphere is that the oceanic sink of mercury may be slightly less important.

Simulations with a complex atmospheric chemistry model have shown results pointing in the same direction. In the lower troposphere the effect of increased temperature on slow-down of Hg oxidation was, comparing to the effect of the reaction rate only, magnified by the fact that Br concentrations decreased significantly in the +5K case. Thus, in a 5K warmer marine boundary layer the Hg⁰ oxidation rate was reduced by 40% resulting in c.a. 15% increase in concentrations of RGM. In higher altitudes the bromine concentrations were much lower, the dominating source was photolysis of halocarbons and there was only small temperature effect on concentrations. The effect of temperature on slow-down of oxidation of Hg⁰ was accordingly less pronounced.

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1 Introduction

The most specific property of mercury regarding long range transport and cycling in the environment is its ability to appear as a gas in the atmosphere. Both anthropogenic and natural mercury emissions constitute to the most part of gaseous elemental mercury (GEM). Hence, 98 % or more of mercury in air is often in the form of GEM. Atmospheric transport of gases is very efficient making the distribution of mercury unique in comparison to other metals that occur as particles in the air. The atmospheric residence time of mercury has been estimated to be around 0.7 - 1.4 year, which is long enough for it to be distributed on hemispherical scales before it eventually is oxidised and deposited to ground and water surfaces. Oxidised mercury (i. e. Hg^{2+}) easily undergoes reduction by biochemical and photolytical processes. Elemental mercury is then regained and may re-emit back to the atmosphere. For example is $\text{Hg}^{2+}_{(\text{aq})}$ in seawater often reduced to elemental mercury to an extent that the surface water becomes supersaturated in respect to dissolved elemental mercury. As a result elemental mercury is emitted from oceans as well as from fresh water lakes. A significant part of mercury deposited on forest and open land areas may also be reduced and re-emitted back to the atmosphere. Reduction and re-emission of mercury extends the effective atmospheric residence time of mercury and thereby enhance transport and exposure to the environment.

Information on emissions and a detailed understanding of the environmental cycling of mercury is critical for the development of relevant and cost-efficient strategies towards reducing the negative impacts of this metal. Emission inventories are used to drive atmospheric chemical-transport and source-receptor models for the distribution of mercury and prediction of deposition rates. An understanding of the different mercury sources is also of importance towards assessing control options since many different mercury sources exist. In addition to anthropogenic point sources, natural sources also exist and mercury once released into the environment can be extensively recycled between different compartments of the environment.

Factors influencing mercury cycling are:

- Natural and anthropogenic emissions
- Atmospheric oxidation and deposition
- Reduction processes and re-emission
- Sinks

Emission inventories based on official statistics and estimations has been made to assess the global anthropogenic emission of mercury (Pacyna et al., 2006; UNEP-report 2009). Estimating natural emissions and re-emission of mercury is difficult, but has been made using global models (Lamborg et al., 2002; Mason and Sheu, 2002; Selin et al., 2007, Strode et al., 2007). According to these findings is the total annual emission of mercury to the atmosphere, including re-emission, 4 to 7 kton per year. Whereof 2.2 - 2.6 kton is due to primary anthropogenic emission, 1 - 2 kton natural emissions and the rest re-emission. Hence, re-emission is thought to be significant and according to some model calculations is the re-emission from the oceans higher than the total primary anthropogenic emission (Mason and Sheu, 2002; Selin et al., 2007, Strode et al., 2007).

Deposition of mercury is closely related to atmospheric oxidation. This is because GEM is a relatively persistent compound with low solubility in rain water and a low dry deposit rate. On the other hand is oxidised mercury, i.e. Hg(II) species, water soluble and also prone for dry deposition. Hg(II) compounds are believed to be formed in the atmosphere via gas phase reactions but also via oxidation in the aqueous phase, i.e. within cloud droplets. However, the exact chemical composition of the oxidation products are not yet known. The gaseous fraction of oxidised mercury is often referred to as "Reactive Gaseous Mercury" (RGM). The term reactive mercury denotes a class of divalent mercury species which, like for example $\text{HgCl}_4^{2-}(\text{aq})$, readily undergo reduction to Hg^0 by Sn^{2+} in diluted HCl solution (a procedure commonly used in the chemical analysis of mercury in water samples). Although not definitely proven, it is likely that RGM constitutes from species like $\text{HgCl}_2(\text{g})$ and $\text{HgBr}_2(\text{g})$ or mixed halides like $\text{BrHgCl}(\text{g})$. The mechanism of atmospheric oxidation of mercury is not fully understood, but gas phase reactions involving the bromine radical has lately achieved great interest among researchers and it has been suggested that reaction (1) may be important.

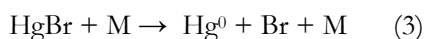


The reaction rate of reaction (1) has been determined in laboratory studies (Sommar et al., 1999; Ariya et al., 2002; Donohoue et al., 2006) and found to be about 3×10^{-13} molecules $\text{cm}^{-3} \text{s}^{-1}$ at room temperature and 1 atm pressure. Donohoue et al., 2006 used a flow reactor with pulsed laser induced fluorescence to simultaneously measure Hg^0 and Br radicals. Both the pressure and temperature dependence of reaction (1) was determined yielding a result consistent with a three-body recombination reaction according to reactions 1. A temperature dependent expression of $(1.46 \pm 0.34) 10^{-32} (\text{T}/298)^{-(1.86 \pm 1.49)} \text{cm}^6 \text{molecule}^{-2} \text{s}^{-1}$ was determined for the third-order recombination rate coefficient in nitrogen buffer gas (Donohoue et al., 2006).

The HgBr radical is formed in reaction (1) may further react to form a stable divalent mercury compound according to reaction (2), which also is a third-order recombination reaction,



or alternatively decompose to Hg^0 and the Br radical according to reaction (3).



At the present no experimental result is published regarding reaction (2) and (3), but according to theoretical calculations, HgBr seems to be a relatively stable radical that does not react with O_2 and has an atmospheric lifetime long enough to undergo further reactions leading to stable RGM-species according to reaction (2) (Goodsite et al., 2004). Reaction rate coefficients for reaction (2) and (3) were calculated to be $2.5 10^{-10} (\text{T}/298)^{-0.57} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ and $1.2 10^{10} e^{(-8357/\text{T})} \text{s}^{-1}$ at 1 atm pressure, respectively. That HgBr actually reacts with Br to form HgBr_2 according to equation (3) has recently also been confirmed experimentally (Hynes A. J., 2008).

As mentioned above divalent mercury in seawater (also denoted dissolved gaseous mercury, DGM) tends to be reduced to elemental mercury. Many investigators have found that DGM formation in coastal seawater and lake water is strongly correlated with solar intensity. Hence, the concentration of DGM often shows a diurnal pattern with peak DGM concentrations in the middle of the day (Amyot et al., 1997; Lanzillotta and Ferrara, 2001; Gårdfeldt et al., 2001, Amyot et al. 2004). There are few investigations regarding diurnal DGM trends in the open sea, but recent observations suggest that it also occur in off shore waters (Andersson et al. 2007). The exact processes behind

reduction of Hg(II) and build up of DGM in surface seawater is not known but it is assumed to be photolytically induced by biotic or abiotic processes or both. Quantitative information on the air-sea exchange of mercury is crucial for understanding the transport and environmental cycling of mercury which in turn are key issues regarding assessment of harmful effects from anthropogenic mercury emissions. According to recent modelling results (global air-sea exchange model by Strode et al., 2007), is the present total deposition of mercury to the oceans be as high as 4.56 kton per year. The deposition input is balanced by an annual emission of 2.82 kton elemental mercury. About 1.74 kton mercury is annually transported to the deep ocean, whereof loss via sediment burial is assumed to be 0.2 kton y^{-1} . Hence, 62% of the deposited mercury is reduced and re-emitted back to the atmosphere, 34% is temporary removed from re-circulation via transport to the deep ocean and 4% is permanently removed from circulation via burial in the sediments.

Re-emission of mercury from the oceans can be parameterised as a function of DGM concentration, water temperature and wind speed, according to the empirical equation by Nightingale (Nightingale et al., 2000; Wanninkhof, 1992).

$$F_{\text{Hg}} = k \times [\text{DGM} - \text{GEM}/H'(T_w)] \quad [1]$$

F_{Hg} is the Hg mass flux per unit surface area and time, $H'(T_w)$ is the unitless Henry's Law (i.e. the DGM - GEM equilibrium coefficient) and k is the so called piston velocity, a kinetic parameter with the unit length per time,

$$k = (0.222 \times u_{10}^2 + 0.333 \times u_{10}) \times (Sc_{\text{Hg}}/660)^{-0.5} \quad [2]$$

where u_{10} is the wind speed 10 m above the sea level and Sc_{Hg} is the Schmidt number. The Schmidt number is a substance specific unitless number defined as the kinematic viscosity of seawater divided by the aqueous diffusivity of the specie being transferred. The $[\text{DGM} - \text{GEM}/H'(T_w)]$ term in equation [1] is the difference between the actual DGM concentration in the seawater and the DGM saturation concentration ($\text{GEM}/H'(T_w)$). When the seawater is supersaturated in respect to DGM the mercury flux is from the sea to the atmosphere and with DGM concentrations less than the saturation level the flux attains the opposite direction. According to equation [1] is the magnitude of the flux a function of the degree of saturation but depends also largely on the k -factor, i. e. the wind speed and the Schmidt number. The seawater temperature influences the flux rate in two ways. The DGM saturation concentration decreases with increasing water temperature due to the temperature dependence of the Henry's Law coefficient and secondly, the Schmidt number decreases with temperature making the k -factor to increase. Hence, an increase in seawater temperatures tend to decrease the maximum solubility of DGM, thereby promoting emission of elemental mercury an effect which also is enhanced by an increasing k -factor.

The boreal forest floor is likely to be an additional sink for mercury. In forested ecosystems, deposition of mercury is often enhanced by a factor of 2-4 in comparison to open field wet deposition. The enhanced deposition is mainly driven by air-canopy interactions. Mercury in the form of RGM and particulate mercury are dry deposited to the forest canopy and then washed off by precipitation or deposited to the forest floor via litter fall (i.e. needles, leaves, branches). Mercury bonds strongly to humus groups in the forest soil. Hence, mercury is known to accumulate in boreal forest soils (Munthe et al., 1998). The Boreal forest belt cover most of inland [Alaska](#), [Canada](#), [Sweden](#), [Finland](#), [Norway](#) and inland [Russia](#) and is the world's largest terrestrial ecosystem. Therefore, substantial amounts of mercury have accumulated in this area during the last century. However, our current understanding on its long-term stability and if it really can be considered as a permanent sink of mercury is still not known.

2 Effects of climate change on mercury oxidation and re-emission

2.1 Atmospheric oxidation of mercury under changed atmospheric temperature profile

An important issue is to what extent cycling of mercury in the future may be altered in regards to climate change. According to predictions made by the IPCC, the Earth's surface temperature may increase by 1 - 5 °C within 100 years from now. How would that impact cycling of mercury and thereby the environmental exposure to mercury? Climate change predictions imply that most of the parameters that determine the global mercury cycle today will change. Given, on one hand, the uncertainties regarding the climate change predictions them self and on the other hand the limitations in our present understanding of the cycling of mercury, this question is obviously very complex and almost impossible to answer, at least in a quantitative manner. Nevertheless this issue will briefly be discussed here focusing on some of the most obvious consequences regarding change in atmospheric oxidation rates and oceanic re-emission.

The atmospheric oxidation mechanism presented above has been used to construct a simple model describing Hg oxidation in the marine troposphere. Vertical temperature and pressure profiles used in the model were calculated using the standard lapse rate of 0.0649 K m⁻¹. Results from calculations with different constant mixing ratios of Br radicals are shown in Figure 1.

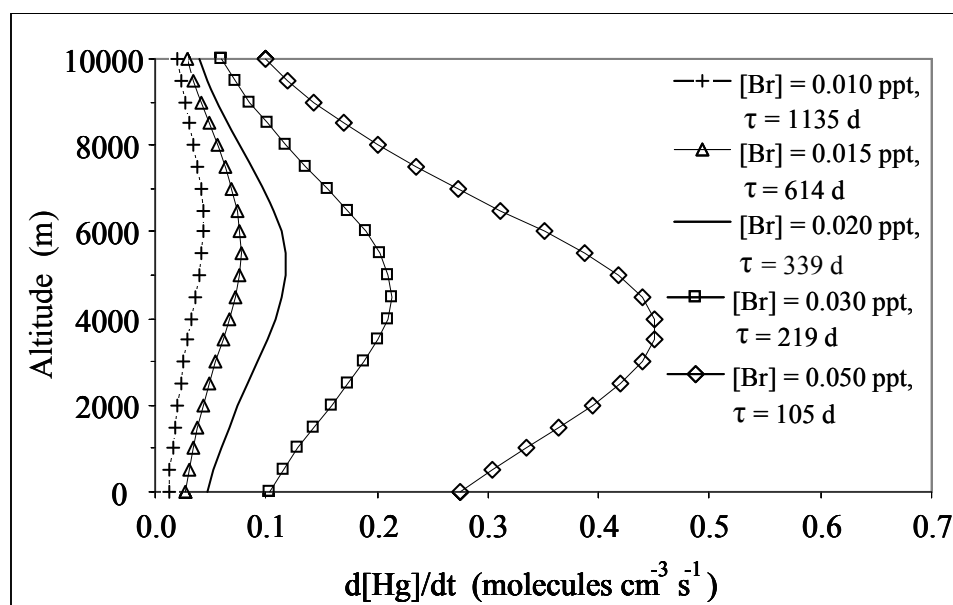


Figure 1. Hg oxidation rates at different constant Br mixing ratios as a function of altitude in the troposphere. A constant Hg mixing ratio of 0.19 ppt was used in all calculations which corresponds to 1.7 ng m⁻³ at sea level. τ denotes lifetime in days.

The reaction rate ($d[\text{Hg}]/dt$) is according to Figure 1 dependent on altitude and reaches a maximum between 4 - 6 km depending on the Br concentration. This is mainly an effect of the strong positive temperature dependence of k_3 . That is, the stability of the HgBr radical is increasing with decreasing temperature and pressure. This effect is also enhanced due to the negative temperature dependence of reaction 1. At higher altitudes the reactivity slows down as an effect of decreasing concentrations of the reactants. The vertical reactivity profiles shown in Figure 1 is likely to be a characteristic of gas phase RGM formation since it must proceed via a recombination reaction forming an intermediate specie similar to HgBr followed by a second recombination reaction. The exact shape of the profile is obviously also dependent on the vertical distribution of Br radicals. For simplicity and due to that the vertical distribution of Br radicals is not exactly known a constant Br mixing ratio was used here. The concentration of Br radicals in the marine troposphere is likely to be less than ≤ 0.1 ppt (Ref). According to the model result a lifetime between 105 to 1135 days is obtained when varying the concentration of Br radicals in the range of 0.5 ppt to 0.01 ppt. To draw definite conclusions regarding the atmospheric lifetime of GEM more data on the temporal and spatial distribution of Br radicals in the marine atmosphere is obviously needed. However, this simple model gives a hint on some important features regarding RGM formation in the atmosphere.

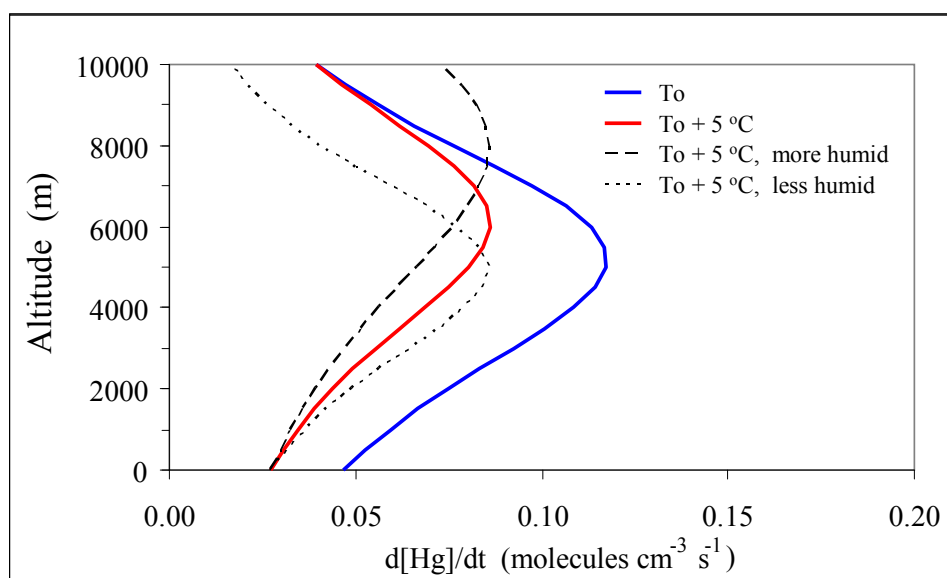


Figure 2. RGM formation in a warmer atmosphere. Blue line: Surface temperature 15 °C, $[\text{Br}] = 0.2$ ppt, GEM concentration 0.19 ppt. Red line: Surface temperature 20 °C, $[\text{Br}] = 0.2$ ppt, GEM concentration 0.19 ppt. Dotted lines corresponds to increased humidity and less humidity, respectively.

The model was also used to test the effect of increased atmospheric temperatures. Figure 2 shows the effect on RGM formation when increasing the surface temperature by 5 °C. Given that everything else is constant the lifetime of GEM will increase from 400 to 560 days. This is entirely an effect of the temperature dependencies of reaction (1-3). Since, a warmer climate also may alter the humidity which in turn changes the vertical temperature and pressure gradients in the troposphere, calculations with a less humid (lapse rate = 0.008 K m^{-1}) and a more humid atmosphere (lapse rate = 0.005 K m^{-1}) were also made. The result is indicated by dotted lines in Figure 2 and shows that with more water vapour in the atmosphere the maximum RGM formation tend to occur at higher altitudes, whereas less humidity will give an opposite effect. A slower conversion of GEM to RGM means increased concentrations of GEM in the atmosphere. However, the real situation is obviously more complex since in a warmer climate other

environmental parameters are likely to change as well. For example, the concentration of many marine atmospheric constituents, including reactants like Br and OH radicals etc., may change thereby altering the gas phase oxidation capacity. Oxidation in heterogeneous phase may also be more important.

2.2 Re-emission of mercury from the ocean – effect of temperature change

The yearly average increase in mercury flux (ΔF_{Hg}) as a consequence of a 5 °C increase in the seawater temperature has been calculated for different initial seawater temperatures and DGM concentrations. The result was obtained using equation [1] and is presented in Figure 3. ΔF_{Hg} values in the range of 1.4 to 6.3 $\mu\text{g m}^{-2} \text{y}^{-1}$ were obtained, at 0 °C initial water temperature and $[\text{DGM}] = 10 \text{ ng m}^{-3}$, and 25 °C initial water temperature and a $[\text{DGM}] = 30 \text{ ng m}^{-3}$, respectively. These values can be compared with 7.8 $\mu\text{g m}^{-2} \text{y}^{-1}$ which is the present yearly average oceanic mercury flux estimated with the global air-sea exchange model by Strode et al., 2007.

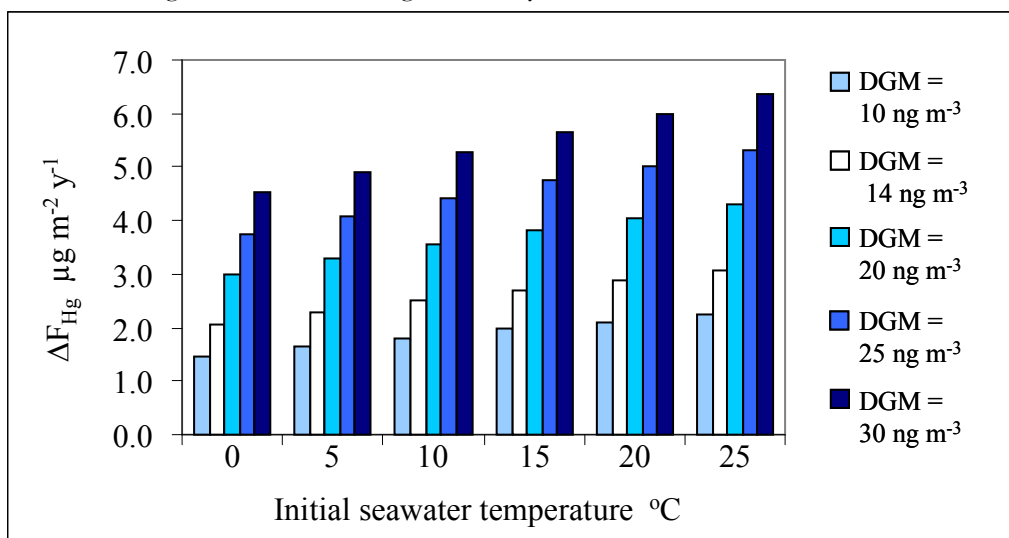


Figure 3. Increase in mercury flux from the ocean surface as a result of a 5 °C increase in the surface water temperature as a function of initial water temperature and DGM concentration. The wind speed was kept constant at 7 m s⁻¹.

The result of Strode et al., predicts the highest DGM concentrations to occur in equatorial surface waters (2 - 130 ng m⁻³). Concentrations > 30 ng m⁻³ may also occur at high latitudes during summer due to high biological activity enhancing reduction of deposited mercury. A mean global oceanic DGM concentration of 14 ng m⁻³ was reported (Strode et al., 2007). Calculation of ΔF_{Hg} as a function of different initial seawater temperatures is considered to mimic the temperature differences at different latitudes. A ΔF_{Hg} value of 2.7 $\mu\text{g m}^{-2} \text{y}^{-1}$, corresponding to an emission increase of 35%, is obtained from the average DGM concentration (14 ng m⁻³) and an initial seawater temperature of 15 °C. According to Figure 3, would the strongest temperature effect be along the equator where both the temperatures and DGM concentrations are high. On the other hand, climate change predictions suggest the strongest temperature increase to occur in polar and near Polar Regions. Hence, the possible increase in mercury flux will also be strongly coupled to the spatial distribution of heat in the oceans.

2.3 Model of multiphase oxidation of coupled to halogen chemistry

Effect of the climate change on oxidation of gaseous mercury has several aspects. As discussed earlier the temperature dependence of the oxidation rate constants may have a significant impact by itself. Change in solubility of the mercury species due to the temperature change and change of liquid water content of atmosphere due to the climate change feedback will lead to change in gas-to-particle distribution of mercury and hence to change in its oxidation pathways. Also changes in atmospheric composition and temperature will also bring changes in mixing ratios of the oxidants important for the mercury oxidation. There are substantial uncertainties in all these processes, some caused by gaps in scientific understanding, others by uncertainties in future emission scenario development. Oxidation pathways of the metallic mercury are only poorly understood, both in the gas and in the aqueous phase. The most recent results indicate that the main oxidation pathway of Hg^0 is via oxidation by atomic Br while oxidation by OH and ozone are of minor importance. However, mixing ratios of atomic Br are vastly unknown. Biogeochemical cycling of bromine involves catalytic release of Br from the sea-salt and its cycling through deliquescent aerosol particles as well as slow oxidation and photolysis of halocarbons emitted by natural and industrial sources. Few measurements of BrO in the marine boundary layer (MBL) found BrO mixing ratios of few ppt(V) (James et al., 2000; Lesser et al., 2003; Saiz-Lopez et al., 2008). The only global modelling study describing distribution of Br in atmosphere was done by Kerkweg et al. (2008). Atmospheric distribution of hydroxyl radical, which can also play a role in Hg^0 oxidation, has been studied through numerous modelling studies and verified by direct measurements on a small scale and by methyl chloroform and ^{14}CO data on large to global scale. According to IPCC (2007) the OH exhibits a strong year-to-year variability with a slightly increasing trend in 80's and decreasing trend in 90's. According to the IPCC's model predictions the OH could change by between -18% and +5% in the 21st century.

In the previous section effect of the climate change on the Hg^0 oxidation was quantified in terms of the effect of the increased temperature on the reaction rates of reactions 1 – 3. In this section we will investigate effects of the temperature increase on the whole tropospheric photochemical system including halogens and mercury and couple the effect of temperature change on Hg^0 oxidation with effects on levels of oxidants and on the solubilities of Hg species in deliquescent aerosol. For this study box model 'MOCCA' (Model Of Chemistry Considering Aerosols) modified to study atmospheric chemistry in the free troposphere has been used.

The chemical mechanism of the model considers gas-phase reactions as well as aqueous-phase reactions in deliquescent sulphate and sea-salt aerosol particles and exchange of volatile soluble species between the two phases. Photochemical reaction rates vary as a function of solar declination. Apart from the standard tropospheric HO_x , CH_4 , and NO_x chemistry, the reaction mechanism includes sulphur, chlorine, bromine, iodine and mercury compounds. Model results were published for the polluted MBL (J. Geophys. Res. 101D, 9121-9138, 1996) as well as for the remote MBL (Nature 382, 327-330, 1996, J. Geophys. Res. 109D, 2004). The model was modified to simulate development of halogen and mercury species in the FT. The air parcel was initiated with concentrations of organic halogens, sulphate particles and sea-salt particles, following development of chemistry in the gas phase and in the 7 particle-size fractions of sea-salt and sulphate aerosol particles. Simulations were performed for altitudes between 0 and 10 km every 2nd km. Mixing ratios used for initialisation of the model is the lowest and highest levels are listed in Table 1. Vertical profiles for temperature, pressure, humidity, initial mixing ratios of species and for aerosol

concentrations were used from simulations of Swedish regional CTM Match. The ‘climate change’ simulations were performed by increasing the temperature by 5K throughout the whole profile. Humidity was not altered in these simulations.

Table 1. Initial mixing ratios used in model simulations

	lower free troposphere	upper troposphere
CH ₃ Br	10 pmol/mol	10 pmol/mol
CHBr ₃	3.5 pmol/mol	0.2 pmol/mol
CH ₂ Br ₂	0.5 pmol/mol	0.5 pmol/mol
sulfate aerosol	3x10 ⁸ m ⁻³	1x10 ⁹ /3x10 ⁸ m ⁻³
sea-salt aerosol	mean summer 2km	mean summer 10 km
HCl (g)	40 pmol/mol	50 pmol/mol
Hg ⁰ (g)	0.18 pmol/mol (1.5 ng/m ³)	0.18 pmol/mol

Mixing ratios of atomic Br at different altitudes of the base-case simulation are shown on Figure 4. A strong decreasing gradient of Br mixing ratios from the sea surface to 6 km is caused by a gradient in sea-salt concentration. For higher altitudes the gradient is much smaller and of opposite sign. Here the major part of bromine comes from oxidation and photodissociation of halocarbons, mainly CHBr₃. These two different processes driving the Br chemistry at different altitudes are reflected also in differences in Br mixing ratios caused by the increase of ambient temperature by 5K. While in the lowest levels the Br mixing ratios are substantially reduced by the temperature increase, at higher levels the change is small and successively changes the sign, i.e. Br mixing ratios increase slightly with increasing temperature at the highest levels (Figure 5). Mixing ratios of BrO reach around 2 ppt(V) during the day-time maxima in the MBL simulation (alt. = 0 km), a value consistent with the MBL measurements, while the BrO mixing ratios in the upper-most level are approximately by factor 10 lower, i.e. reach 0.2 ppt(V) in maxima. Figure 6 shows Br/BrO ratio for 3 different levels. Effect of the temperature change on the OH mixing ratios is very small.

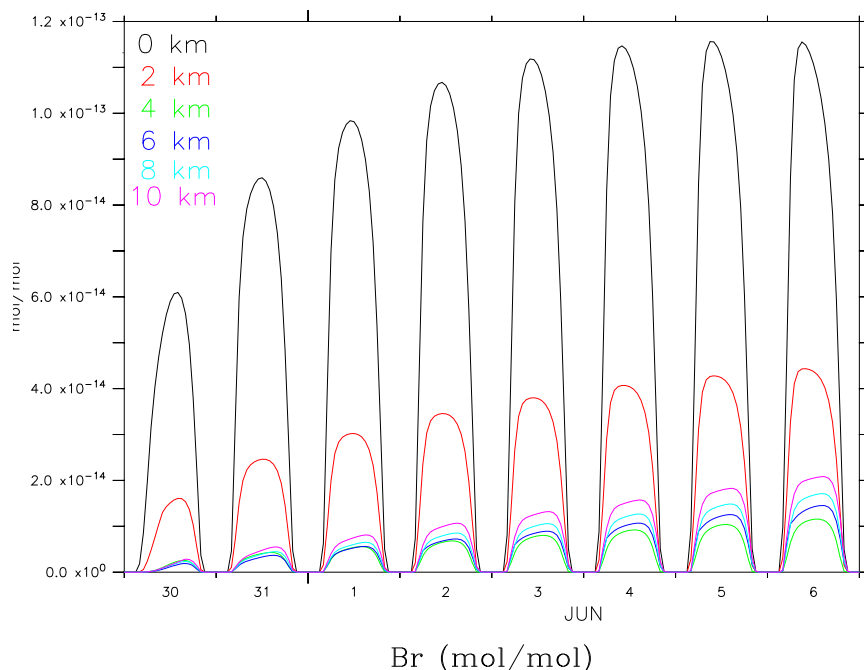


Figure 4. Mixing ratios of Br at 6 different altitude levels in the Base-case simulation

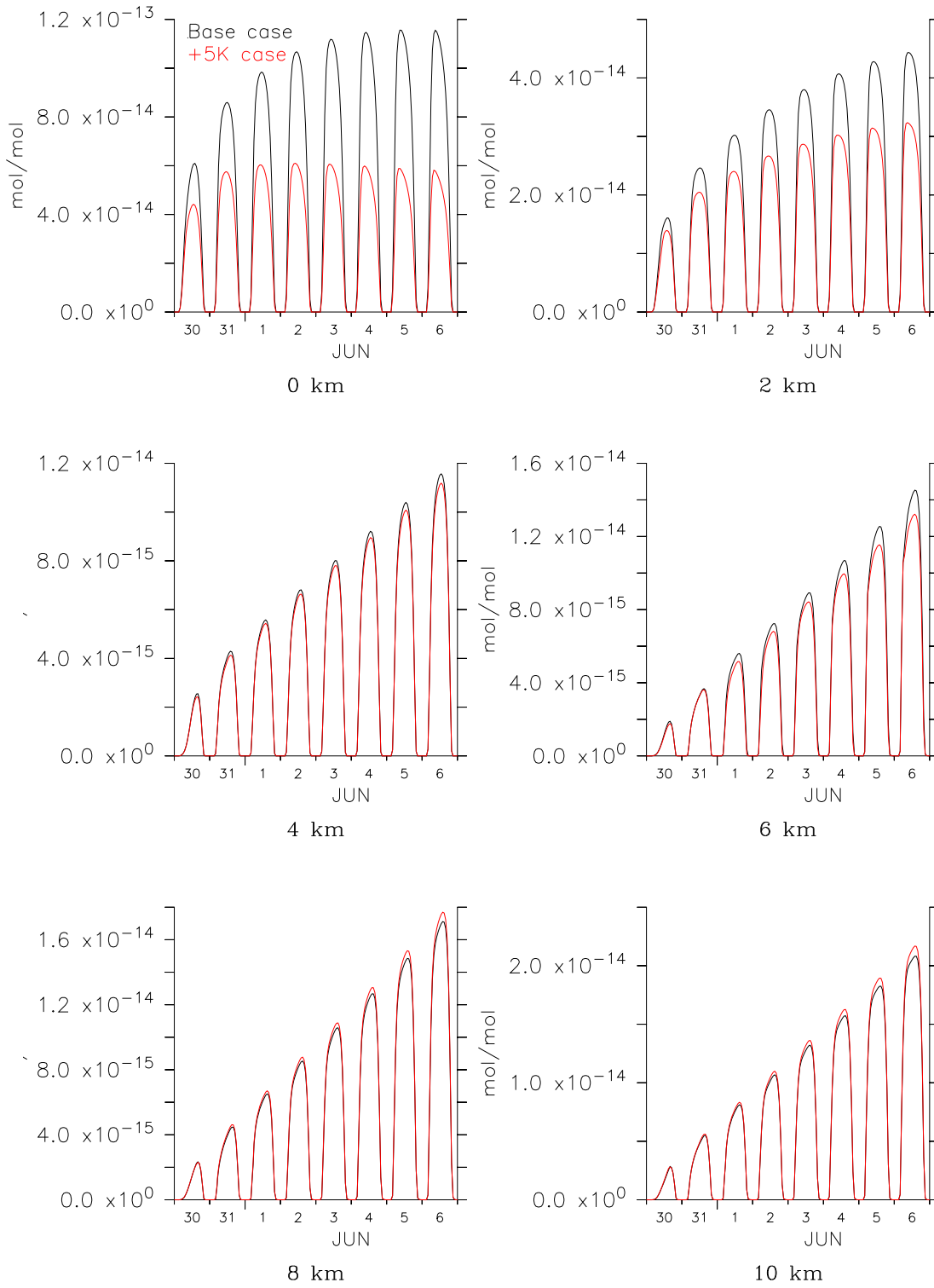


Figure 5. Br mixing ratios at different altitude levels in base-case (black) and +5K case (red) simulations.

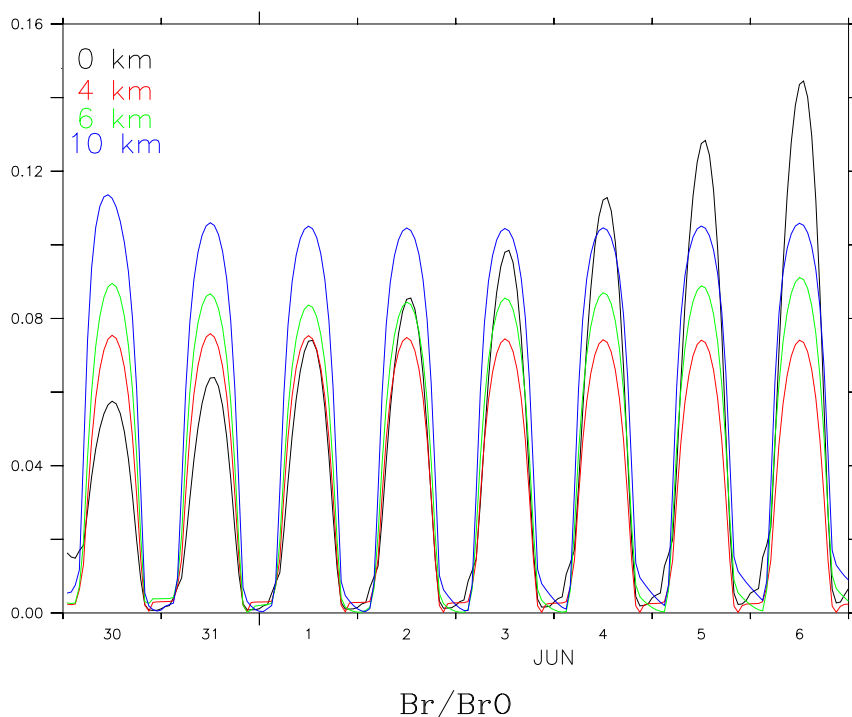


Figure 6. Ratios of the Br/BrO mixing ratios in the Base-case run at 0 km-, 4 km-, 6km- and 10 km-altitude.

Mercury species

In the model the Hg^0 is oxidized in the gas phase through reactions with ozone, OH, H_2O_2 , Cl and Br. The oxidation by Br has been described in the previous section, other 4 reactions use the low limit of the rate estimates:

$$\begin{aligned} k(\text{Hg}^0 + \text{O}_3) &= 3.0 \cdot 10^{-18} \cdot e^{(-1407/T)}, k(\text{Hg}^0 + \text{O}_3)_{295} = 2.55 \cdot 10^{-20} \\ k(\text{Hg}^0 + \text{OH}) &= 3.55 \cdot 10^{-14} \cdot \text{EXP}(294/\text{TEMP}) \cdot 0.5, k(\text{Hg}^0 + \text{OH})_{295} = 4.8 \cdot 10^{-14} \\ k(\text{Hg}^0 + \text{H}_2\text{O}_2) &= 4.0 \cdot 10^{-19} \\ k(\text{Hg}^0 + \text{Cl}) &= 1.0 \cdot 10^{-12} \end{aligned}$$

Figure 7 shows mixing ratio of Hg^0 oxidized during 24 h by the individual reactions at sea-level and at 10-km altitude. We can see that with the used reaction rates the Hg^0 oxidation is dominated by the Br reaction at sea level and by the OH reaction at the tropopause level. This fact is reflected into Hg^0 mixing ratios at different altitude levels depicted in Figure 8 and to the effects of temperature changes on the Hg^0 oxidation rates. At lower altitudes the oxidation is dominated by the sea-salt-derived Br and the temperature increase results into lower Br mixing ratios and into lower reaction rate constant of the net $\text{Hg}^0 + \text{Br}$ oxidation, both leading to the decreased rate of oxidation. In upper troposphere the increase in temperature does not have the same impact on Br as this is mostly derived from halocarbon oxidation and photolysis and further, due to much lower Br mixing ratios the oxidation is dominated by OH and this reaction has negative temperature dependence. Due to this the oxidation rates in the model of upper troposphere are slightly higher in

warmer case. The simulated mixing ratios of RGM and the individual oxidized species at 0-km altitude are shown in Figure 9. In the model RGM is dominated by HgBr in nighttime while HgO peaks in the daytime. This diurnal variation is result of variation of the gas-phase production and the gas-to particle transport. In the +5K case the HgBr production is lower and HgO thus becomes more important part in the simulated RGM. The RGM mixing ratios at the +5K-case are by ca. 25% lower than in the base case. At 8-km altitude the simulated RGM is dominated by HgO (Figure 10). The peak mixing ratios are somewhat higher than at the ground level, however the average values are similar due to more pronounced diurnal variation at high altitude. At 8-km altitude the warmer scenario has lower RGM mixing ratios by approximately 20%, similar to the simulated sea-level conditions (Figure 10).

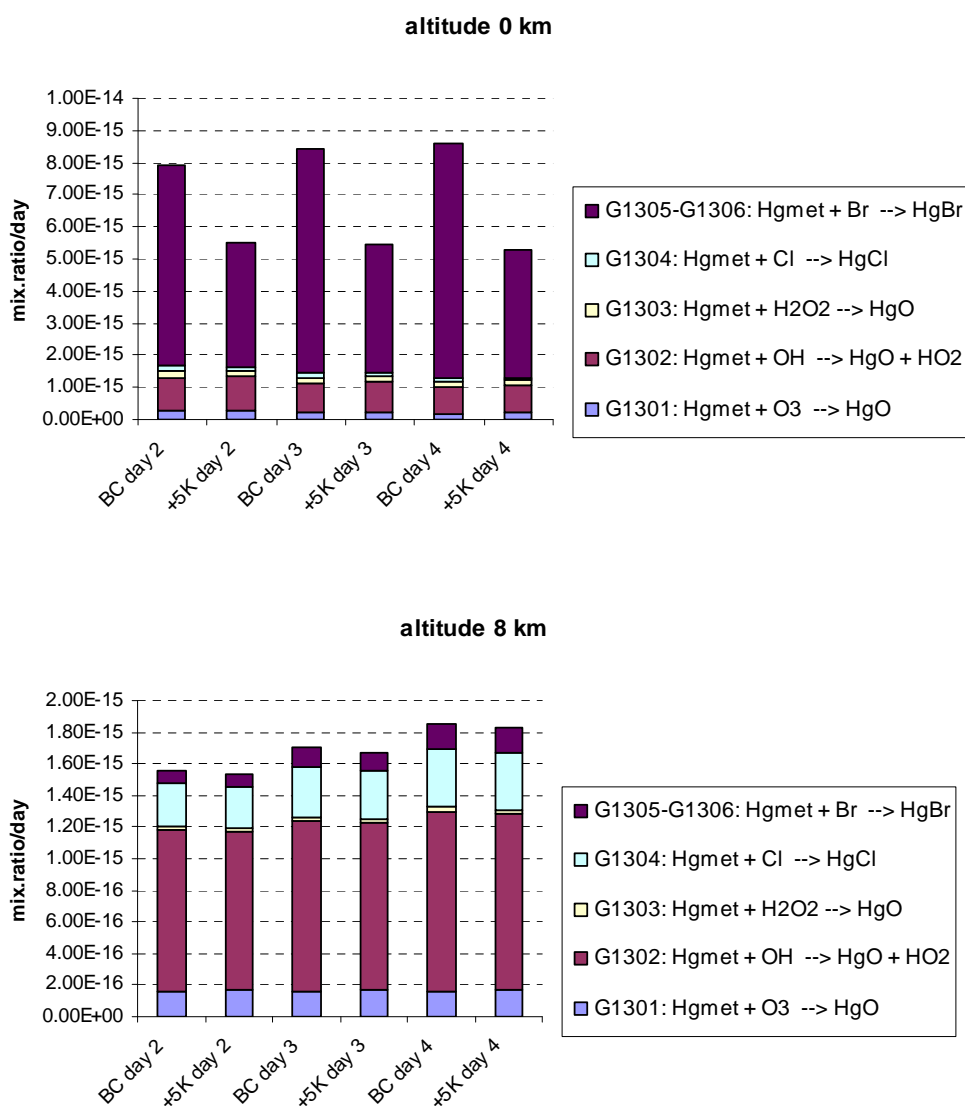


Figure 7. Rates (in mix. ratio/day, 1ppt = 1.0E-12) of Hg⁰ oxidation in the gas phase at sea-level (upper panel) and at 10-km altitude (bottom panel). The 2nd, 3rd and 4th day of simulation are depicted for the base-case and for the +5K-case

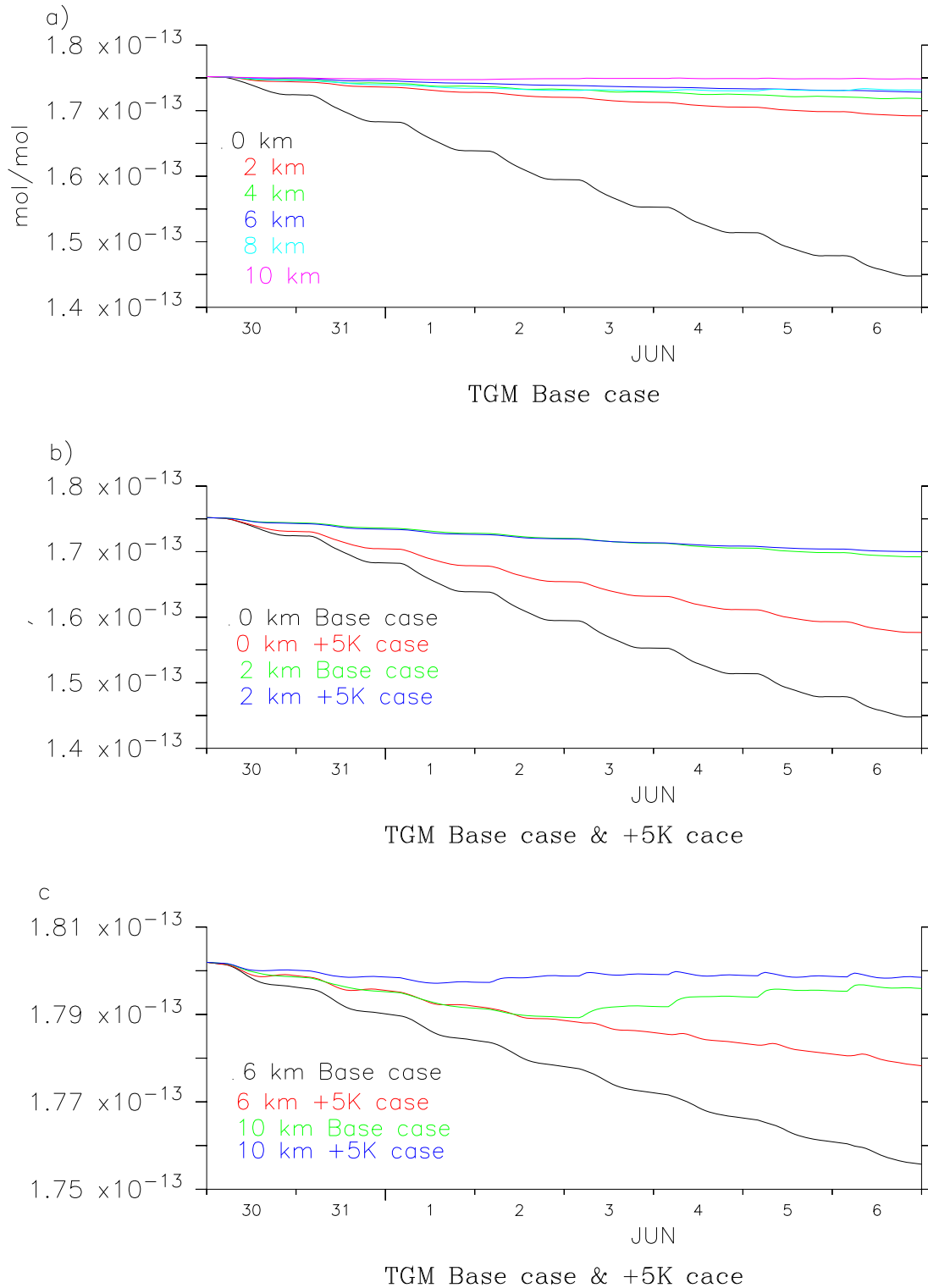


Figure 8. Gaseous Hg^0 in model simulations. a) – the base-case simulation. b) and c) – comparison of Hg^0 in the base-case and in +5K simulation (note different scales on y-axis).

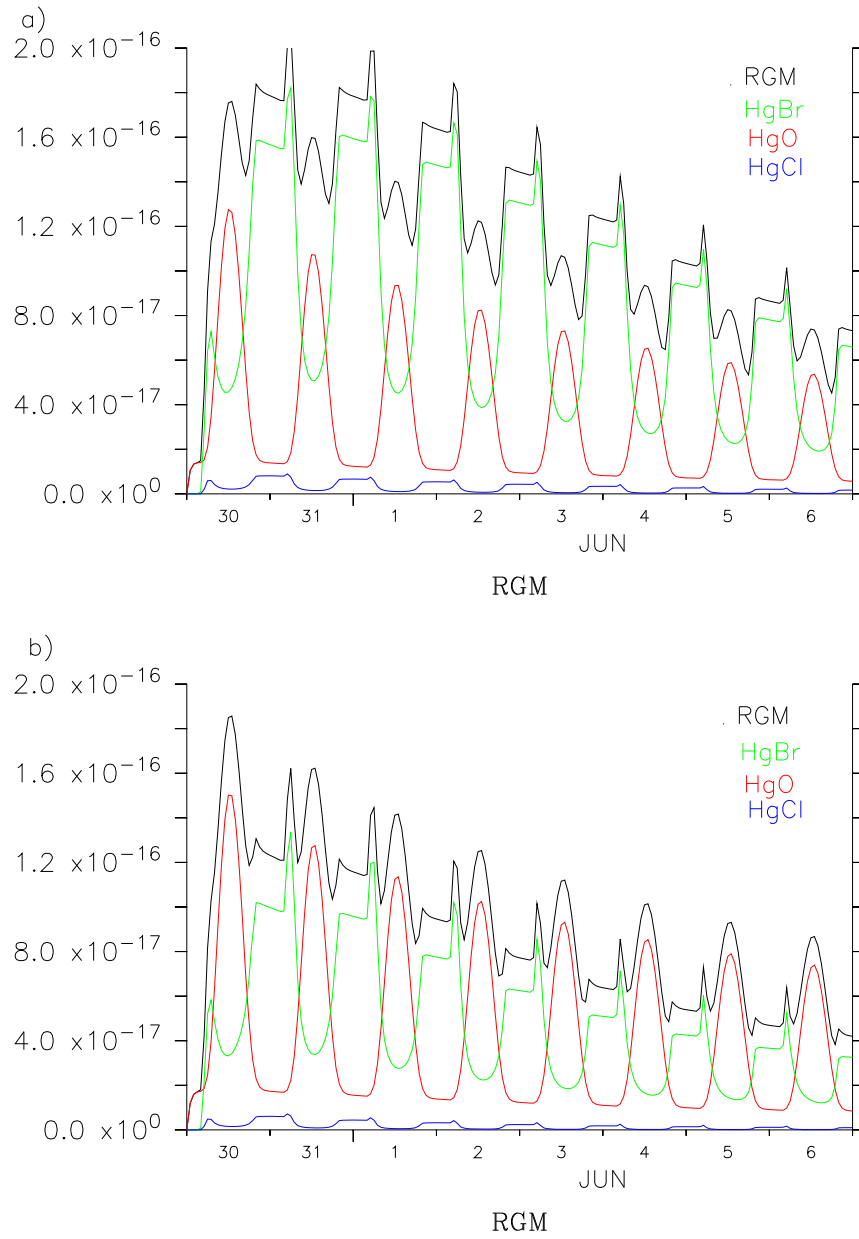


Figure 9. Total RGM (black) and the oxidized-mercury species in the base-case (top) and +5K-case (bottom) simulations at 0 km-altitude.

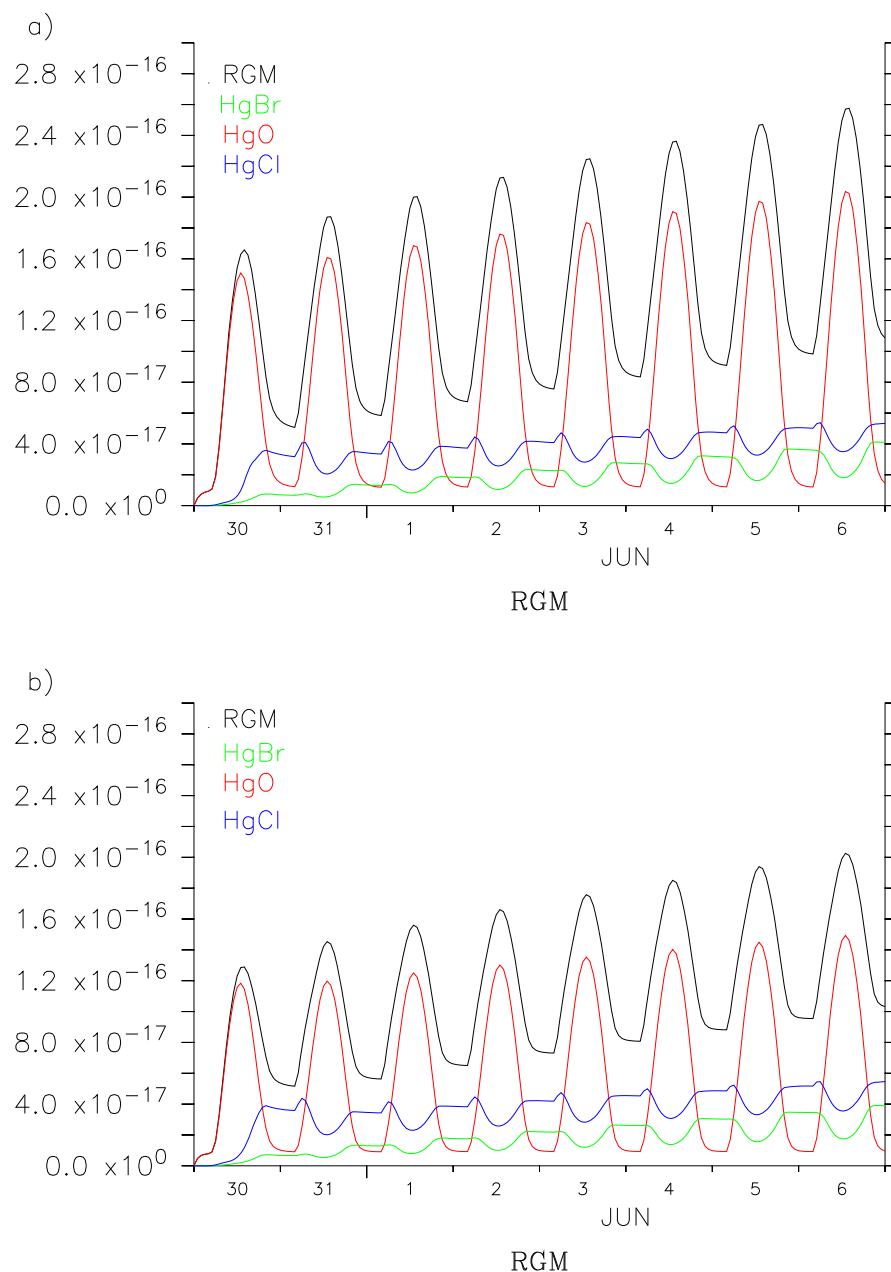


Figure 10. Total RGM (black) and the oxidized-mercury species in the base-case (top) and +5K-case (bottom) simulations at 8 km-altitude.

In aqueous phase most of Hg is in form of HgCl_4^{2-} in the sea-salt aerosol and HgCl_2 and HgBrCl in the sulphate aerosol. In the MBL the increased temperature does not have significant effect on dissolved Hg^0 (Figure 11), however, concentrations of the dissolved divalent mercury decreases by c.a. 25% (by 0.002 ppt) in the sea-salt aerosol and by 50% (by 0.01 ppt) in the sulphate aerosol. Dissolved mercury in the upper troposphere is shown on Figure 12. The mixing ratios are lower, however by far not proportionally to the aerosol concentration at that altitude. The +5K case has more dissolved Hg than the base case.

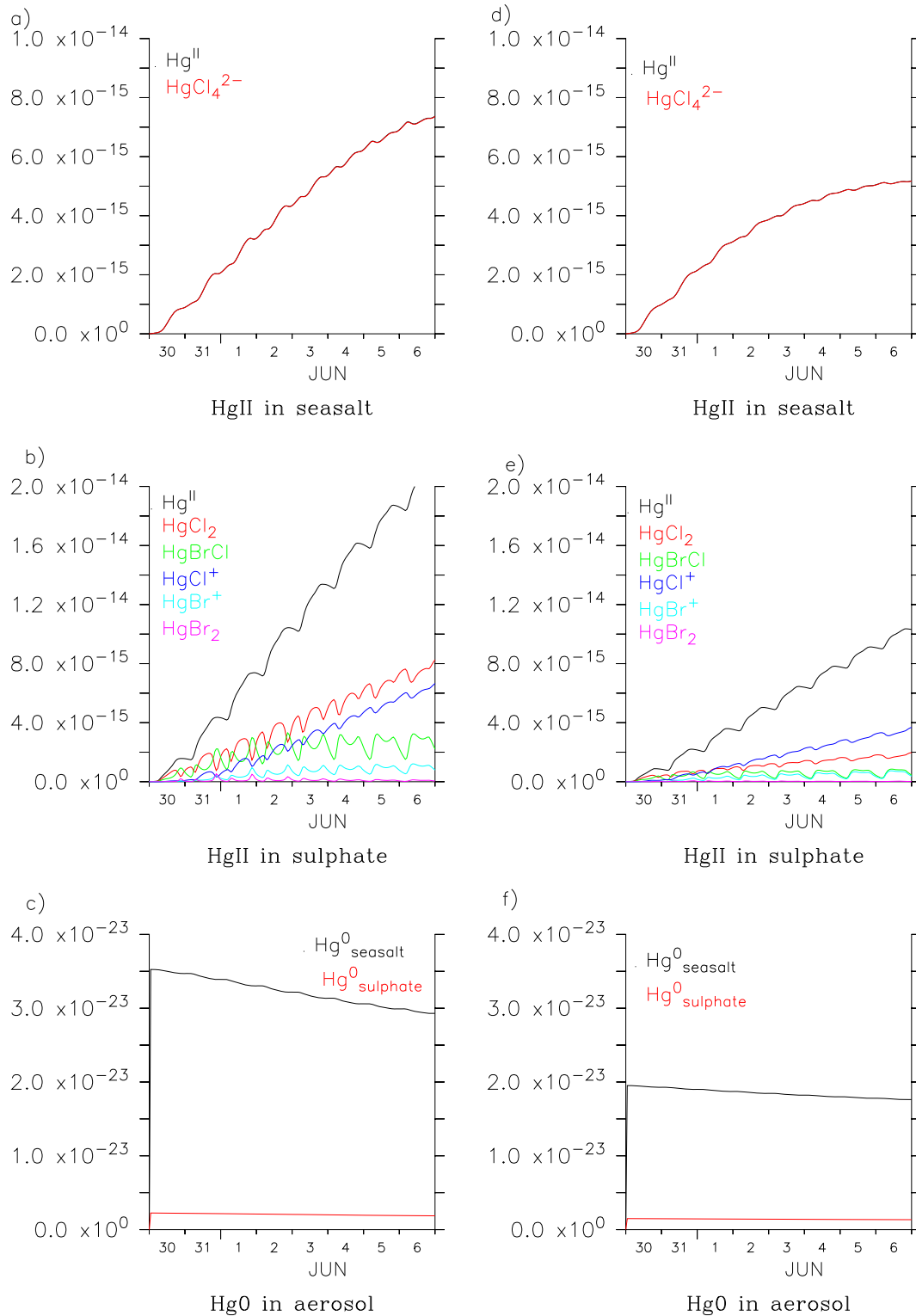


Figure 11. Dissolved Hg^{II} in sea-salt (upper panels) and sulphate (middle panels) aerosol in the MBL (altitude 0 km). Dissolved Hg^0 in sea-salt and sulphate aerosol (lower panels). Left column – base-case, Right column - +5K-case.

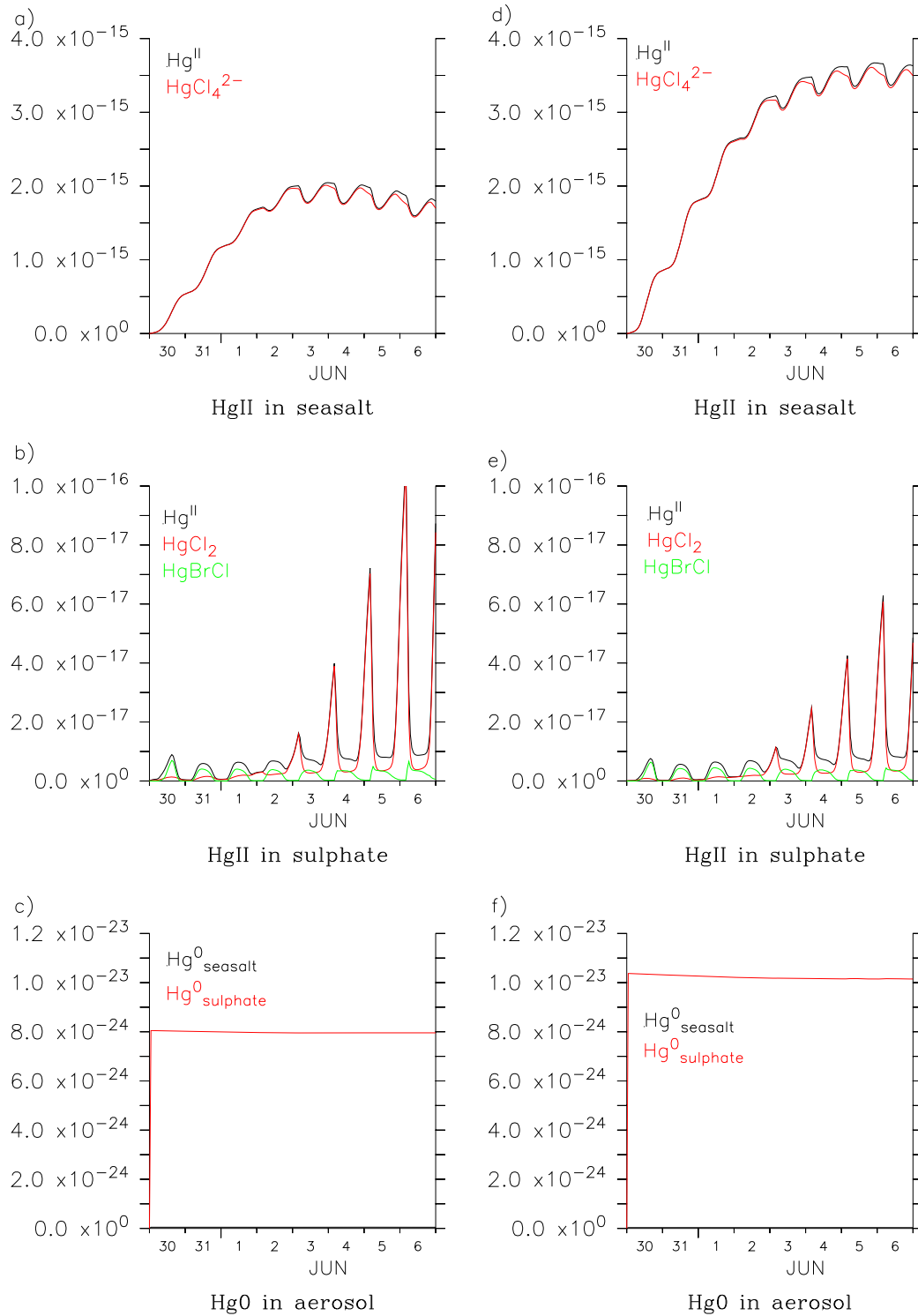


Figure 12. Dissolved Hg^{II} in sea-salt (upper panels) and sulphate (middle panels) aerosol in upper troposphere (altitude 8 km). Dissolved Hg^0 in sea-salt and sulphate aerosol (lower panels). Left column – base-case, Right column - +5K-case.

3 Conclusions

A simple model has been used to evaluate the possible effect of climate change in respect to changed atmospheric oxidation potential of mercury. Only the effect of temperature increase was considered to elucidate effect of changed Hg^0 oxidation rate only. The result suggests that in a warmer climate gas phase oxidation of GEM in the marine troposphere may be less efficient causing the mercury concentration in the atmosphere to increase.

Simulations with a complex atmospheric chemistry model have shown results pointing in the same direction. In the lower troposphere the effect of increased temperature on slow-down of Hg oxidation was, comparing to the effect of the reaction rate only, magnified by the fact that Br concentrations decreased significantly in the +5K case. Thus, in a 5K warmer marine boundary layer the Hg^0 oxidation rate was reduced by 40% resulting in c.a. 15% increase in concentrations of RGM. In higher altitudes the bromine concentrations were much lower, the dominating source was photolysis of halocarbons and there was only small temperature effect on concentrations. The effect of temperature on slow-down of oxidation of Hg^0 was accordingly less pronounced.

A simple model of re-emission of Hg^0 from the oceans has shown that simultaneously as the mercury oxidation rates decreases with increasing temperature, re-emission flux from the ocean to the atmosphere tends to increase. If this really is the case it means that part of the oceanic mercury pool will be moved to the atmosphere. The environmental effect of that not obvious. A somewhat higher GEM concentration is not harmful as such, but means that mercury distribution via the atmosphere could be even more important in the future. Another conceivable consequence of mercury being moved from the sea to the atmosphere is that the oceanic sink of mercury may be slightly less important.

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