

Atmospheric chemistry of Hg (standard O₃/OH version)

Mercury transformations in the atmosphere include transitions between the gaseous, aqueous and solid phases, chemical reactions in the gaseous and aqueous environment. Hereafter we shall use the term “aqueous phase” for all species dissolved in cloud water and those in composition of solid particles suspended in a droplet. Besides, we shall distinguish three main mercury forms in the atmospheric air: gaseous elemental mercury (GEM), total particulate mercury (TPM) and reactive gaseous mercury (RGM).

Inter-phase equilibrium

All gaseous mercury compounds are soluble to some extent in cloud- and rainwater. Size of cloud droplets is small enough to establish the equilibrium between the solution and the gas rather rapidly. The equilibrium described by Henry’s law has pronounced temperature dependence. The expression for the Henry’s law constants (in the form of the ratio of a species concentration in liquid to its air concentration, M·cm³/molec) are given by:

$$H = A_H T \exp \left[B_H \left(\frac{T_0}{T} - 1 \right) \right], \quad (1)$$

where $T_0 = 298.15$ K; coefficients A_H and B_H for gaseous mercury forms and other gases of interest are presented in Table 1.

Table 1. Coefficients of Henry’s law constants

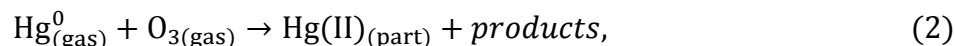
Compound	A_H	B_H	Reference
Hg ⁰	$1.76 \cdot 10^{-23}$	9.08	<i>Andersson et al., 2004</i>
HgCl ₂	$1.75 \cdot 10^{-16}$	18.75	<i>Ryaboshapko et al., 2001</i>
O ₃	$1.58 \cdot 10^{-24}$	7.8	<i>Sander, 1997</i>
·OH	$3.41 \cdot 10^{-21}$	17.72	<i>Jacobson, 1999</i>
Cl ₂	$4.48 \cdot 10^{-16}$ *		<i>Lin and Pehkonen, 1999</i>

* - no temperature dependence is available

Besides, we expect that half of particulate mercury mass in cloud- and rainwater is represented by soluble compounds [*Brosset and Lord, 1991; Fitzgerald et al., 1991; Lamborg et al., 1995*]. On the other hand, it is assumed that all mercury mass in the aqueous phase is transformed to the particulate form if the cloud droplet is evaporated.

Gas-phase reactions

One of the most important gas phase reactions is oxidation of elemental mercury by ozone:



Since, ozone is always in plenty under ordinary atmospheric conditions this second-order reaction is described by a first-order rate expression with the reaction rate constant depending on the reactant concentration:

$$R_1 = \frac{d[\text{Hg}_{(\text{gas})}^0]}{dt} = k'_1[\text{Hg}_{(\text{gas})}^0], \quad (3)$$

$$k'_1 = k_1[\text{O}_{3(\text{gas})}], \quad k_1 = A \exp(-E_a/(R_{\text{univ}}T)),$$

where $A = 2.1 \cdot 10^{-18} \text{ cm}^3/(\text{molec}\cdot\text{s})$ [Hall, 1995];

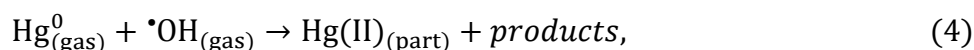
$$E_a = 10.36 \text{ kJ/mole};$$

$$R_{\text{univ}} = 8.31 \text{ J}/(\text{mole}\cdot\text{K});$$

$[\text{O}_{3(\text{gas})}]$ is ozone concentration, molec/cm³.

It is believed that the product of the reaction – mercury oxide is in particulate form due to its poor volatility [Sommar et al., 2001; Schroeder and Munthe, 1998].

Recently investigated reaction of mercury oxidation by hydroxyl radical in gaseous phase is expected to be very significant or even prevailing sink of elemental mercury in the troposphere [Sommar et al., 1999; 2001; Pal and Ariya, 2004]:

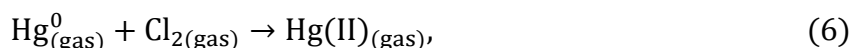


$$R_2 = -\frac{d[\text{Hg}_{(\text{gas})}^0]}{dt} = k'_2[\text{Hg}_{(\text{gas})}^0], \quad k'_2 = k_2[\bullet\text{OH}_{(\text{gas})}], \quad (5)$$

where $k_2 = 8.7 \cdot 10^{-14} \text{ cm}^3/(\text{molec}\cdot\text{s})$ [Sommar et al., 2001];

$[\bullet\text{OH}_{(\text{gas})}]$ is hydroxyl radical concentration, molec/cm³.

Gas phase oxidation of elemental mercury by chlorine can be noticeable in the ocean boundary layer during nighttime [Seigneur et al., 1994; Tokos et al., 1998; Ariya et al., 2002]:



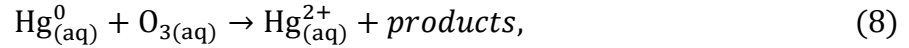
$$R_3 = -\frac{d[\text{Hg}_{(\text{gas})}^0]}{dt} = k'_3[\text{Hg}_{(\text{gas})}^0], \quad k'_3 = k_3[\text{Cl}_{2(\text{gas})}], \quad (7)$$

where $k_3 = 2.6 \cdot 10^{-18} \text{ cm}^3/(\text{molec}\cdot\text{s})$ [Ariya et al., 2002];

$[\text{Cl}_{2(\text{gas})}]$ is chlorine concentration, molec/cm³.

Aqueous-phase reactions

Dissolved elemental mercury is oxidized by ozone producing mercury oxide Hg^0 , which is very short-lived in the liquid phase and is rapidly transformed to the mercury ion $\text{Hg}_{(\text{aq})}^{2+}$. Thus, the resulting reaction can be written as follows:



with the reaction rate expression:

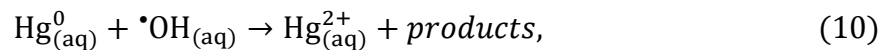
$$R_4 = -\frac{d[\text{Hg}_{(\text{aq})}^0]}{dt} = k'_4[\text{Hg}_{(\text{aq})}^0], \quad k'_4 = k_4 H_{\text{O}_3}[\text{O}_{3(\text{gas})}], \quad (9)$$

here $k_4 = 4.7 \cdot 10^7 \text{ M}^{-1}\text{s}^{-1}$ [Munthe, 1992];

$[\text{O}_{3(\text{gas})}]$ is ozone concentration, molec/cm³;

H_{O_3} is Henry's constant for ozone.

Another important reaction of mercury oxidation in aqueous phase is reaction with hydroxyl radical:



Reaction rate expression for this reaction has the following form:

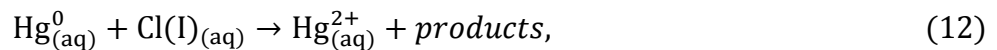
$$R_5 = -\frac{d[\text{Hg}_{(\text{aq})}^0]}{dt} = k'_5[\text{Hg}_{(\text{aq})}^0], \quad k'_5 = k_5 H_{\text{OH}}[\bullet\text{OH}_{(\text{gas})}], \quad (11)$$

where $k_5 = 2.4 \cdot 10^9 \text{ M}^{-1}\text{s}^{-1}$ [Gårdfeldt et al., 2001];

$[\bullet\text{OH}_{(\text{gas})}]$ is hydroxyl radical concentration, molec/cm³;

H_{OH} is Henry's constant for hydroxyl radical.

Elemental mercury in aqueous phase is also oxidized by dissolved chlorine Cl(I)_{aq} with formation of mercury ion $\text{Hg}_{(\text{aq})}^{2+}$:



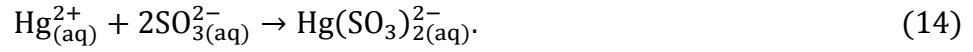
$$R_6 = -\frac{d[\text{Hg}_{(\text{aq})}^0]}{dt} = k'_6[\text{Hg}_{(\text{aq})}^0], \quad k'_6 = k_6 H_{\text{Cl}_2}[\text{Cl}_{2(\text{gas})}], \quad (13)$$

where $k_6 = 2 \cdot 10^6 \text{ M}^{-1}\text{s}^{-1}$ [Lin and Pehkonen, 1999];

$[\text{Cl}_{2(\text{gas})}]$ is chlorine concentration, molec/cm³;

H_{Cl_2} is Henry's constant for chlorine.

Mercury ion $\text{Hg}_{(\text{aq})}^{2+}$ reacts in the solution with sulphite ions SO_3^{2-} resulting in the formation of mercury sulphite complex $\text{Hg}(\text{SO}_3)_2^{2-}$ [Pleijel and Munte, 1995]:

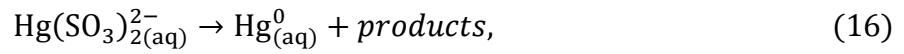


The reaction rate is determined by the air concentration of SO_2 and the cloud water pH:

$$R_7 = -\frac{d[\text{Hg}_{(\text{aq})}^{2+}]}{dt} = k'_7[\text{Hg}_{(\text{aq})}^{2+}], \quad k'_7 = k_7[\text{SO}_{2(\text{gas})}]^2 \cdot 10^{4\text{pH}}, \quad (15)$$

where $k_7 = 1.1 \cdot 10^{-21} \text{ s}^{-1}$, and $[\text{SO}_{2(\text{gas})}]$ is in ppbv. In all calculations we use fixed value for cloud water pH = 4.5.

The sulphite complex $\text{Hg}(\text{SO}_3)_2(\text{aq})^{2-}$ is dissociated to mercury sulphite HgSO_3 , which is unstable, and is readily reduced to $\text{Hg}_{(\text{aq})}^0$. Thus, the reduction process can be described as:



with the reaction rate expression:

$$R_8 = -\frac{d[\text{Hg}(\text{SO}_3)_2(\text{aq})^{2-}]}{dt} = k_8[\text{Hg}(\text{SO}_3)_2(\text{aq})^{2-}], \quad (17)$$

where $k_8 = 4.4 \cdot 10^{-4} \text{ s}^{-1}$.

This process increases the amount of dissolved elemental mercury in a droplet hampering further dissolution of gaseous mercury. Hence, the scheme implies negative feedback controlling elemental mercury uptake from the air.

Mercury ion $\text{Hg}_{(\text{aq})}^{2+}$ also takes part in a number of reactions leading to the formation of various chloride complexes $\text{Hg}_m\text{Cl}_m(R_9)$. These reversible reactions in the first approximation can be replaced by equilibrium concentrations of free mercury ions and mercury in the aggregate of chloride complexes ($[\text{HgCl}^+]$, $[\text{HgCl}_2]$, $[\text{HgCl}_3^-]$, $[\text{HgCl}_4^{2-}]$). The equilibrium ratio of the appropriate mercury concentrations depends upon water content of chloride ion $[\text{Cl}^-]$ and is defined as follows [Lurie, 1971]:

$$r_1 = \frac{[\text{Hg}_n\text{Cl}_m(\text{aq})]}{[\text{Hg}_{(\text{aq})}^{2+}]} = \frac{[\text{Cl}_{(\text{aq})}^-]}{1.82 \cdot 10^{-7}} + \frac{[\text{Cl}_{(\text{aq})}^-]^2}{6.03 \cdot 10^{-14}} + \frac{[\text{Cl}_{(\text{aq})}^-]^3}{8.51 \cdot 10^{-15}} + \frac{[\text{Cl}_{(\text{aq})}^-]^4}{8.51 \cdot 10^{-16}}, \quad (18)$$

The chloride ion concentration in cloud water is taken as $7 \cdot 10^{-5} \text{ M}$ [Acker *et al.*, 1998]. Sulphite and chloride complexes in the aqueous phase can be adsorbed and desorbed by soot particles (R_{10}, R_{11}). Comparatively fast equilibrium of these two reverse processes can also be described by means of "dissolved-to-adsorbed ratio". Based on the appropriate reaction rates it could be taken equal to 0.2 in both cases [Petersen *et al.*, 1998]:

$$r_2 = - \frac{[\text{Hg}(\text{SO}_3)_2^-(\text{aq})]}{[\text{Hg}(\text{SO}_3)_2^-(\text{soot})]} = \frac{[\text{Hg}_n\text{Cl}_m(\text{aq})]}{[\text{Hg}_n\text{Cl}_m(\text{soot})]} \approx 0.2. \quad (19)$$

Summary of all chemical transformations of mercury included into the model is presented in Table 2.

Table 2. Summary of mercury transformations included into the model

Reactions and equilibriums	k or H	Units	Reference
$\text{Hg}_{(\text{gas})}^0 + \text{O}_{3(\text{gas})} \rightarrow \text{Hg}(\text{II})_{(\text{part})} + \text{products}$	$2.1 \cdot 10^{-18} \exp(-1247/T)$	$\text{cm}^3/(\text{molec} \cdot \text{s})$	Hall, 1995
$\text{Hg}_{(\text{gas})}^0 + \cdot\text{OH}_{(\text{gas})} \rightarrow \text{Hg}(\text{II})_{(\text{part})} + \text{products}$	$8.7 \cdot 10^{-14}$	$\text{cm}^3/(\text{molec} \cdot \text{s})$	Sommar et al., 2001
$\text{Hg}_{(\text{gas})}^0 + \text{Cl}_{2(\text{gas})} \rightarrow \text{Hg}(\text{II})_{(\text{gas})}$	$2.6 \cdot 10^{-18}$	$\text{cm}^3/(\text{molec} \cdot \text{s})$	Ariya et al., 2002
$\text{Hg}_{(\text{aq})}^0 + \text{O}_{3(\text{aq})} \rightarrow \text{Hg}_{(\text{aq})}^{2+} + \text{products}$	$4.7 \cdot 10^7$	$\text{M}^{-1}\text{s}^{-1}$	Munthe, 1992
$\text{Hg}_{(\text{aq})}^0 + \cdot\text{OH}_{(\text{aq})} \rightarrow \text{Hg}_{(\text{aq})}^{2+} + \text{products}$	$2.4 \cdot 10^9$	$\text{M}^{-1}\text{s}^{-1}$	Gårdfeldt et al., 2001
$\text{Hg}_{(\text{aq})}^0 + \text{Cl}(\text{I})_{(\text{aq})} \rightarrow \text{Hg}_{(\text{aq})}^{2+} + \text{products}$	$2 \cdot 10^6$	$\text{M}^{-1}\text{s}^{-1}$	Lin and Pehkonen, 1999
$\text{Hg}_{(\text{aq})}^{2+} + 2\text{SO}_3^{2-}(\text{aq}) \rightarrow \text{Hg}(\text{SO}_3)_2^-(\text{aq})$	$1.1 \cdot 10^{-21} [\text{SO}_2(\text{gas})]^2 \cdot 10^{4pH^*}$	s^{-1}	Petersen et al., 1998
$\text{Hg}(\text{SO}_3)_2^-(\text{aq}) \rightarrow \text{Hg}_{(\text{aq})}^0 + \text{products}$	$4.4 \cdot 10^{-4}$	s^{-1}	Petersen et al., 1998
$\text{Hg}_n\text{Cl}_m(\text{aq}) \leftrightarrow \text{Hg}_{(\text{aq})}^{2+}$	$f([\text{Cl}^-])^{**}$	1	Lurie, 1971
$\text{Hg}_n\text{Cl}_m(\text{aq}) \leftrightarrow \text{Hg}_n\text{Cl}_m(\text{soot})$	0.2	1	Petersen et al., 1998
$\text{Hg}(\text{SO}_3)_2^-(\text{aq}) \leftrightarrow \text{Hg}(\text{SO}_3)_2^-(\text{soot})$	0.2	1	Petersen et al., 1998
$\text{Hg}_{(\text{gas})}^0 \leftrightarrow \text{Hg}_{(\text{aq})}^0$	$1.76 \cdot 10^{-23} T \exp(9.08(T_0/T-1))$	$\text{M} \cdot \text{cm}^3/\text{molec}$	Andersson et al., 2004
$\text{HgCl}_{2(\text{gas})} \leftrightarrow \text{HgCl}_{2(\text{aq})}$	$1.75 \cdot 10^{-16} T \exp(18.75(T_0/T-1))$	$\text{M} \cdot \text{cm}^3/\text{molec}$	Ryaboshapko et al., 2001
$\text{O}_{3(\text{gas})} \leftrightarrow \text{O}_{3(\text{aq})}$	$1.58 \cdot 10^{-24} T \exp(7.8(T_0/T-1))$	$\text{M} \cdot \text{cm}^3/\text{molec}$	Sander, 1997
$\cdot\text{OH}_{(\text{gas})} \leftrightarrow \cdot\text{OH}_{(\text{aq})}$	$3.41 \cdot 10^{-21} T \exp(17.72(T_0/T-1))$	$\text{M} \cdot \text{cm}^3/\text{molec}$	Jacobson, 1999
$\text{Cl}_{2(\text{gas})} \leftrightarrow \text{Cl}(\text{I})_{(\text{aq})}$	$4.48 \cdot 10^{-16}$	$\text{M} \cdot \text{cm}^3/\text{molec}$	Lin and Pehkonen, 1999

* - $[\text{SO}_2(\text{gas})]$ is in ppbv

** - see Equation (18)

As it was mentioned above one can distinguish three groups of mercury compounds being in equilibrium. The first group (*A*) contains elemental mercury in the gaseous and dissolved phase; the second one (*B*) consists of the mercury sulphite complex both dissolved and on soot particles; and the third group (*C*) includes free mercury ions, mercury chloride complexes dissolved and adsorbed by soot particles and gaseous mercury chloride:

$$\begin{aligned}
 A &= \text{Hg}_{(\text{gas})}^0 + \text{Hg}_{(\text{aq})}^0, \\
 B &= \text{Hg}(\text{SO}_3)_2^-(\text{aq}) + \text{Hg}(\text{SO}_3)_2^-(\text{soot}) \\
 C &= \text{Hg}_{(\text{aq})}^{2+} + \text{Hg}_n\text{Cl}_m(\text{aq}) + \text{Hg}_n\text{Cl}_m(\text{soot}) + \text{HgCl}_{2(\text{gas})}
 \end{aligned} \quad (20)$$

According to this simplified scheme and introduced notations mercury transformations in the liquid phase are described by the following system of the first-order differential equations:

$$\begin{cases} \frac{d[A]}{dt} = -\alpha(k'_4 + k'_5 + k'_6)[A] + \beta k_8[B], \\ \frac{d[B]}{dt} = -\beta k_8[B] + \gamma k'_7[C], \\ \frac{d[C]}{dt} = -\gamma k'_7[C] + \alpha(k'_4 + k'_5 + k'_6)[A]. \end{cases} \quad (21)$$

Here $\alpha = H_{\text{Hg}}C_w/(\rho_w + H_{\text{Hg}}C_w)$ is the fraction of mercury in the A group corresponding to the dissolved form; ρ_w is water density; C_w is cloud liquid water content defined as mass of cloud water per unit volume. Parameter $\beta = r_2/(1 + r_2)$ denotes mercury fraction of the B group in the dissolved phase. Value $\gamma = r_2r_3/(r_1r_3 + r_2r_3 + r_1r_2)$ is the fraction of mercury in the C group corresponding to the mercury ion $\text{Hg}_{(\text{aq})}^{2+}$. Parameter $r_3 = H_{\text{HgCl}_2}C_w/(\rho_w + H_{\text{HgCl}_2}C_w)$ is the fraction of mercury chloride HgCl_2 in cloud water. The analytical solution of the equations system with appropriate initial conditions defines mercury evolution in the aqueous phase during one time step.

- Acker K, Moller D, Wieprecht W., Kalass D., Auel R. [1998] Investigations of ground-based clouds at the Mt. Brocken. Fresenius. *Anal. Chem.* **361**, 59-64.
- Andersson M., Wängberg I., Gårdfeldt K., Munthe J. [2004] Investigation of the Henry's low coefficient for elemental mercury. Proceedings of the 7th Conference "Mercury as a global pollutant". RMZ – Materials and Geoenvironment, Ljubljana, June 2004.
- Ariya P.A., Khalizov A., Gidas A. [2002] Reactions of gaseous mercury with atomic and molecular halogens: kinetics, product studies, and atmospheric implications. *J. Phys. Chem.* **106**, 7310-7320.
- Brosset C., Lord E. [1991] Mercury in precipitation and ambient air – a new scenario. *WASP***56**, 493-506.
- Fitzgerald W.F., Mason R.P., Vandal G.M. [1991] Atmospheric cycling and air-water exchange of mercury over mid-continental lacustrine regions. *WASP***56**, 745-767.
- Gårdfeldt K., Sommar J., Strömberg D., Feng X. [2001] Oxidation of atomic mercury by hydroxyl radicals and photoinduced decomposition of methylmercury in the aqueous phase. *Atmos. Environ.* **35**, 3039-3047.
- Hall B. [1995] The gas phase oxidation of mercury by ozone. *WASP***80**, 301-315.
- Jacobson M. Z. [1999] *Fundamentals of atmospheric modeling*. Cambridge University Press. 656 p.
- Lamborg C. H., Fitzgerald W. F., Vandal G. M., Rolffhus K. R. [1995] Atmospheric mercury in northern Wisconsin: sources and species. *WASP***80**, 189-198.
- Lin C.-J., Pehkonen S. O. [1999] The chemistry of atmospheric mercury: a review. *Atmos. Environ.* **33**, 2067-2079.
- Lurie Yu. Yu. [1971] *Handbook for Analytical Chemistry*. Khimiya, Moscow, 454 p.
- Munthe J. [1992] The aqueous oxidation of elemental mercury by ozone. *Atmos. Environ.* **26A**, 1461-1468.
- Pal B., Ariya P. [2004] Atmospheric transformation of elemental mercury upon hydroxyl radicals under near tropospheric conditions. Proceedings of the 7th Conference "Mercury as a global pollutant". RMZ – Materials and Geoenvironment. Ljubljana, June 2004.
- Petersen G., Munthe J., Pleijel K., Bloxam R. and A.V.Kumar [1998] A comprehensive Eulerian modeling framework for airborne mercury species: Development and testing of the tropospheric chemistry module (TCM). *Atmos. Environ.* **32**(5), 829-843.
- Pleijel K., and Munte J. [1995] Modeling the atmospheric mercury cycle - chemistry in fog droplets. *Atmos. Environ.* **29**, 1441-1457.
- Ryaboshapko A., Ilyin I., Bullock R., Ebinghaus R., Lohman K., Munthe J., Petersen G., Segneur C., Wangberg I. [2001] Intercomparison study of numerical models for long-range atmospheric transport of mercury. Stage I:

- Comparison of chemical modules for mercury transformations in a cloud/fog environment. EMEP/MSC-E Technical report 2/2001, Meteorological Synthesizing Centre – East, Moscow, Russia.
- Sander R. [1997] Henry's law constants available on the Web. *EUROTRAC Newsletter* **18**, 24-25 (www.mpch-mainz.mpg.de/~sander/res/henry).
- Schroeder W. H. and Munthe J. [1998] Atmospheric mercury - an overview. *Atmos. Environ.* **32**, 809-822.
- Seigneur C., Wrobel J. and Constantinou E. [1994] A chemical kinetic mechanism for atmospheric inorganic mercury. *Environ. Sci. and Technol.* **28**(9), 1589-1597.
- Sommar J., Gårdfeldt K., Feng X., Lindquist O. [1999] Rate coefficients for gas-phase oxidation of elemental mercury by bromine and hydroxyl radicals. In: Mercury as a Global Pollutant. 5th International Conference, May 23-28, 1999, Rio de Janeiro, Brazil. Book of abstracts, p. 87.
- Tokos J. J. S., Hall B., Calhoun J. A., and Prestbo E. M. [1998] Homogeneous gas-phase reaction of Hg⁰ with H₂O₂, O₃, CH₃I, and (CH₃)₂S: implications for atmospheric Hg cycling. *Atmos. Environ.* **32**, 823-827.