Towards an advanced description and modelling of the atmospheric multiphase chemistry of mercury: CAPRAM HG module 1.0

Erik Hoffmann[1],Tao Li[2], Andreas Tilgner[1], Yan Wang[2], and Hartmut Herrmann[1]

[1] Leibniz Institute for Tropospheric Research (TROPOS), Atmospheric Chemistry Department (ACD), Leipzig, Germany
[2] School of Environmental Science and Engineering, Shandong University, Qingdao 266237, China

contact: erik.hoffmann@tropos.de

Introduction and Motivation

Mercury is a neurotoxic element emitted predominantly in its less-reactive form as gaseous elemental mercury (GEM) into the atmosphere by various natural and anthropogenic processes. Once emitted it undergoes chemical processing in the atmospheric gas and aqueous phase. There, GEM is oxidised into gaseous oxidised mercury (GOM), which partitions into aerosol particles residing there as particulate bounded mercury (PBM) due to its much higher solubility. The faster deposition of GOM and PBM compared to GEM is of special environmental importance, because they can be converted into more toxic organic mercury in aquatic environments and then take serious place in the food web. Thus, it is crucial for models to understand the transformation of GEM into GOM and PBM and vice versa. To date, numerous gas-phase chemistry simulations were performed, but reveal missing oxidation and reduction processes. However, only few models exist that investigate the multiphase mercury chemistry in a detailed manner.
Therefore, a comprehensive multiphase mercury chemistry mechanism, the CAPRAM HG module 1.0 (CAPRAM-HG1.0), has been developed. The HG1.0 includes 75 gas-phase reactions, 22 phase transfers and 80 aqueous-phase reactions. It was coupled to the multiphase chemistry mechanism MCMv3.2/CAPRAM4.0[(1)] and the extended CAPRAM halogen module 3.0 (CAPRAM-HM3.0)[(2)] for investigations of multiphase Hg chemistry under Chinese polluted conditions. Simulations were performed for summer conditions in 2014[(3)] using the air parcel model SPACCIM[(4)] to investigate the performance of the model to simulate typical concentrations and patterns of GEM, GOM and PBM.
Under non-cloud conditions, model results reveal good coincides with concentrations and patterns for GEM, GOM and PBM measured in China. However, the simulations also show that there are still high uncertainties in atmospheric mercury chemistry. Especially, the complexation with HULIS within aerosol particles needs evaluation as the simulations indicate this process as key process driving concentrations and patterns of both GOM and PBM. Further, the present study demonstrates the need of a better understanding of continental concentrations of reactive halogen species and particle bounded halides as well as their link to the multiphase chemistry and atmospheric cycling of mercury.

Development of the mechanism and model setup

Development of the multiphase Hg chemistry mechanism

- Development from intense literature screening
- Inclusion of newly derived gas-phase photolysis of halogenated mercury[(5,6,7)]
- Consideration of aqueous-phase processing in much more detail as in previous studies

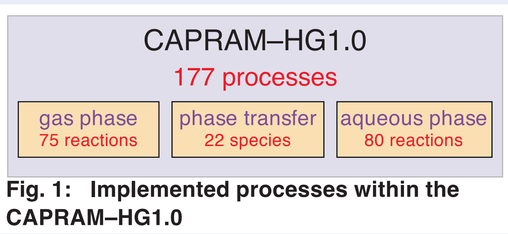

Fig. 1: Implemented processes within the CAPRAM–HG1.0

- Treatment of aqueous-phase photolysis of Hg complexed with oxalic acid[(8)] and HULIS

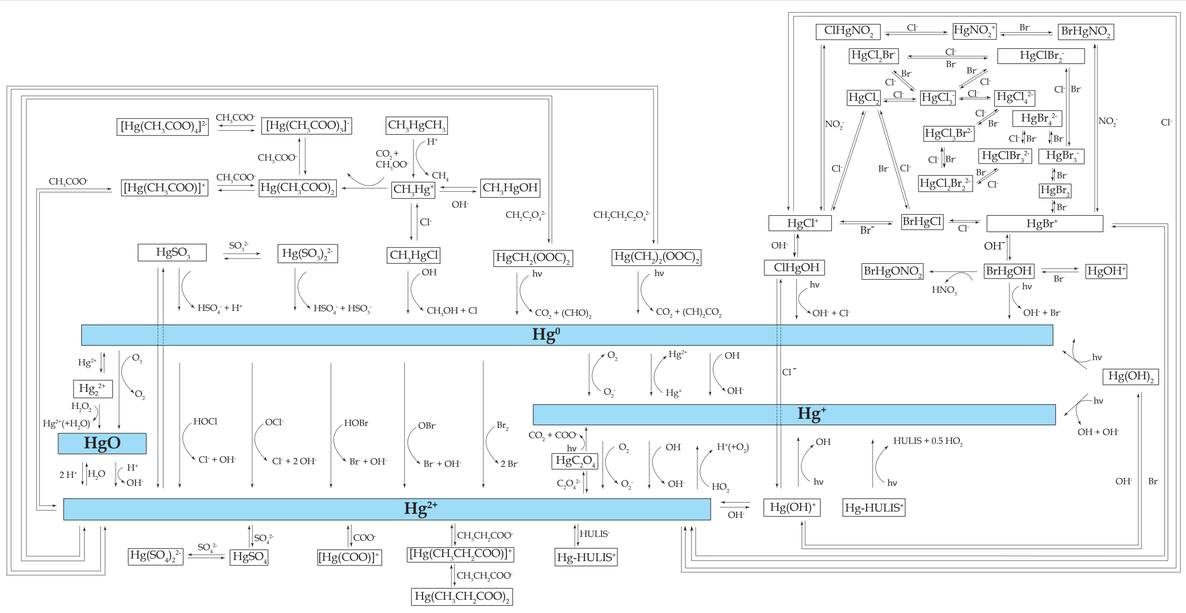

Fig. 2: Representation of Hg aqueous-phase chemistry within CAPRAM–HG1.0.

Setup of multiphase chemistry simulations

- Evaluation simulation for Chinese summertime conditions at Mt Tai[(3)] under cloud-free conditions that run at 90% rel. humidity and for 108 hours
- Emission of Hg(0) and Hg(II) for China[(9)]
- High variability of complex constants for Hg with DOM
- Sensitivity analysis by variation of the Hg-HULIS complex constants within the evaluation simulations (Table 1)

Table 1: Performed sensitivity simulations with different complexation constants for Hg-HULIS.

Simulation	log K	Remarks	Reference
K0	0	no complexation assumed to test impact	
K50	5	conditional stability constant	(10)
K107	10.7	binding to oxygen functional groups	(11)
K118	11.8	binding to hydrophobic fraction	(12)
K144	14.4	cysteine	(13)
K167	16.7	average of Hg-carboxylate complexes	(14)
K200	20	upper bound	upper bound

Preliminary simulation results

Comparison of modelled GEM, GOM and PBM with oberservations

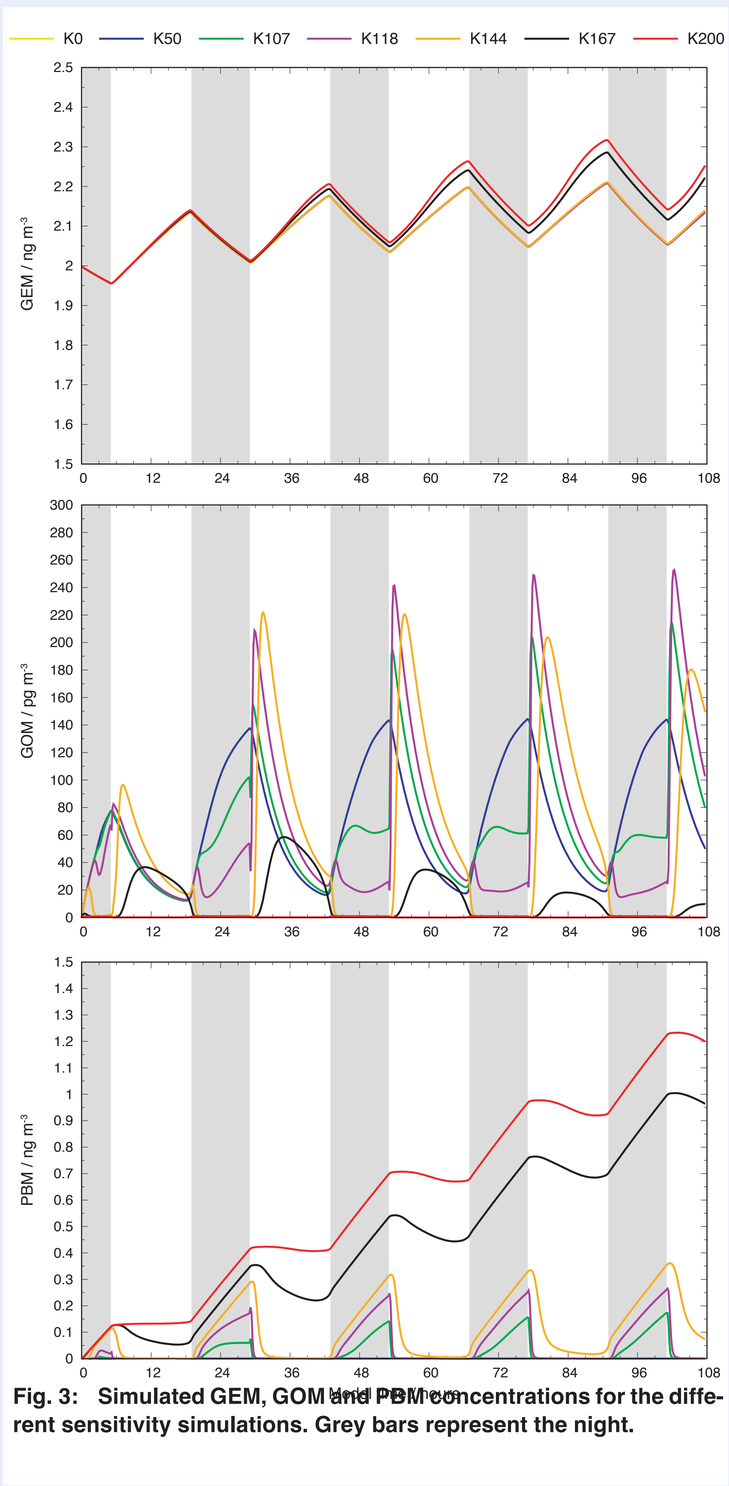

Fig. 3: Simulated GEM, GOM and PBM concentrations for the different sensitivity simulations. Grey bars represent the night.

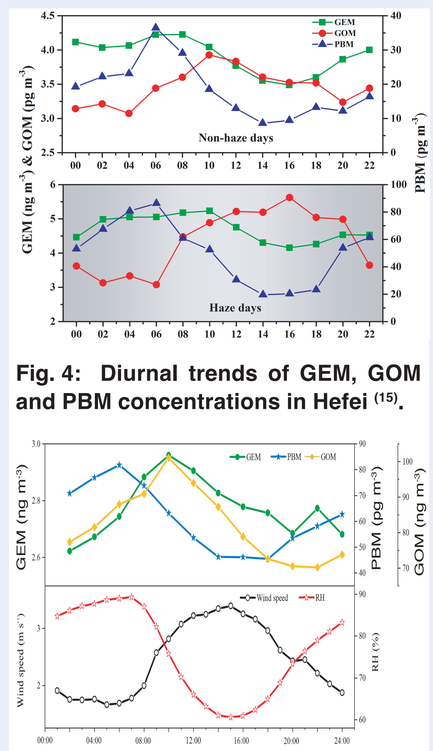

Fig. 4: Diurnal trends of GEM, GOM and PBM concentrations in Hefei [(15)].

Fig. 5: Annual mean diurnal variation in GEM, PBM, and GOM concentrations in Shanghai [(16)].

- Stable GEM concentrations around 2.1 ng m^{-3} modeled in every simulation
- Modeled GOM concentration in simulation K0 of 2.2 ng m^{-3} (far too high) and in K200 < 1 pg m^{-3} (far too low) revelaing the importance of Hg-HULIS complexes on GOM
- Modeled GOM concentration profile fits to measurements only for simulation K167
- Decreasing GOM during simulation time, because of halide depletion in particles
- PBM time profile fits best for simulation K167, but PBM concentrations at upper range of measurements

Summary and Outlook

- Development of a multiphase Hg chemistry mechanism
- Evaluation of the mechanism by box model studies
- Good representation of GEM and GOM, but slightly higher concentrations of PBM
- Formation of Hg-HULS complex is important for model results
- Further activities:
  (i) Further investigation of Hg-HULIS complexation constant impacts
  (ii) Investigating the influence of cloud chemistry
  (iii) Simulations of measurement campaign at Mt. Tai in 2015 and comparison

References

(1) Bräuer, P. et al. (2019), Atmos. Chem. Phys., 19, 9209–9239; (2) Hoffmann, E. H. et al. (2019), Earth Space Chem., 3, 2452–2471; (3) Zhu, Y. et al.(2020), Atmos. Chem. Phys., 20, 6725–6747; (4) Wolke, R. et al. (2005); Atmos. Environ., 39, 4375–4388; (5) Saiz-Lopez, A. (2018), Nature Comm., 9, 4796; (6) Saiz-Lopez, A. (2019), J. Am. Chem. Soc., 41, 8698–8702; (7) Frances-Monerris, A. (2020), Angew. Chem. Int. Ed. 2020, 59, 7605;(8) Gardfeldt, K. & Jonsson, M. (2003), J. Phys. Chem., 107, 4478-4482; (9) Wu, Q. et al. (2016), Environ. Sci. Technol., 50, 13428-13435; (10) Wu, F. et al. (2004), Biogeochemistry, 71, 339-351; (11) Haitzer, M. et al. (2002), Environ. Sci. Technol., 36, 3564-3570; (12) Benoit, J. M., et al. (2001), Geochim. Cosmochim. Acta, 65, 4445-4451, (13) Ravichandran, M. (2004), Chemosphere, 555, 319-331; (14) He, F. (2012), Sci. Total Environ., 416, 429-435; (15) Hong, Q. et al. (2016), Atmos. Chem. Phys., 16, 13807–13821; (16) Qin, X. et al. (2019), Atmos. Chem. Phys., 19, 5923–5940.