Tropospheric Multiphase Chemistry with RACM / CAPRAM2.4

A contribution to the sub-project CMD-MPM

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Model description

Tropospheric multiphase cloud chemistry was simulated with a box model with a constant temperature (288.15 K), pressure (1 atm) and liquid water content (0.3 g_{aq} m_g^{-3}); the droplet distribution was assumed as monodispersed with a droplet radius of 10 µm leading to a droplet concentration of 130 droplets per cm_g^{-3}.

First results for urban conditions were shown from the updated and revised version 2.4 of the Chemical Aqueous Phase Radical Mechanism (CAPRAM) and compared to those of the former version 2.3 (Herrmann *et al.*, 1999). The whole mechanism includes the gas phase mechanism RACM with 237 reactions (Stockwell *et al.*, 1997) and 78 species in the gas phase. For 34 species the uptake is formulated using the resistance model (Schwartz, 1986) considering gas phase diffusion, mass accommodation and Henry's Law coefficients. In CAPRAM2.3 the aqueous phase mechanism includes 236 reactions, in the revised version it is extended to 375 reactions. Major revisions were made in the chemistry of the transition metal ions (TMI), considering reactions of iron, manganese and copper ions. Most of the additional 24 reactions in this part of the mechanism are reduction processes of the ferryl ion (FeO^{2+}) to Fe(III) (Jacobsen *et al.*, 1997 and 1998). The update of the oxidation of organic species lead to a doubling of the number of reactions (from 50 to 108). On the one hand the former formulation of the oxidation of C_1 and C_2 organic species by radical and radical anions (OH, NO_3, Cl_2^-, Br_2^-, SO_4^- and CO_3^-) was split into elementary steps considering all alkyl and peroxyl radicals, on the other hand the C_2 chemistry was completed including the oxidation of dicarbonic species glyoxal, glyoxylic acid and oxalate/ oxalic acid. Whereas the nitrogen, sulfur, chlorine bromine and carbonate chemistry has changed only a few, 27 equilibria were included (in total 58) representing now the highly dynamic coupling of TMI forming hydroxo and iron oxalato complexes. Furthermore in the aqueous phase the photolysis processes of NO_3 and of the iron(III)oxalato complexes being a reduction pathway for iron were added.

First results of CAPRAM2.4

Ferrous and ferric ions

A comparison of the concentration levels of Fe^{2+} and $Fe(OH)^{2+}$ (= Fe(III) species with the highest concentration) in both versions of CAPRAM shows essential differences, although the initial concentration of Fe^{3+} was set to $5\cdot10^{-6}$ M in both simulations. Whereas in CAPRAM2.3 the iron is totally reduced in the first time steps by Cu+, the ferrous ion in CAPRAM2.4 shows only at night a maximum ($2\cdot10^{-6}$ M), during day time the ferric ion reaches this concentration level. The causes of this oxidation/ reduction coupling of the iron are additional effective source processes for Fe^{3+}. On the one hand the reactions of the ferryl ion with H_2O, $HCOO^-$ and Fe^{2+} have a contribution of about 15% to the total production and on the other hand the decay of $FeCH_3O_2^{2+}$ (the adduct between Fe^{2+} and CH_3O_2) to Fe^{3+} forms more than 40 % of the Fe^{3+} at noon.

Glyoxal chemistry

Another topic in the update of the mechanism is the oxidation of glyoxal. It is transported from the gas phase into the droplet where it exists in its hydrated form. The oxidation by radicals lead to glyoxylic acid and in another oxidation step to oxalic acid. For clarify the effectivity of these oxidation pathways two simulations were made: In the first one an initial concentration of oxalate was assumed ($5 \cdot 10^{-6}$ M, equal as that of Fe^{3+} (Sedlak and Hoigné, 1993)), in the other no initial concentration of oxalate was assumed. In both simulations the same hydrogen oxalate concentration of about 10^{-7} M was reached at the second day indicating that this level is really caused by the oxidation of glyoxal. However, the oxidation of given oxalate takes place so rapidly that it is consumed some hours after starting the simulation. Glyoxal in its hydrated form has an aqueous phase maximum concentration of 10^{-10} M at noon. Its diurnal variation is related to that in the gas phase. On the one hand an initial concentration of glyoxal of 0.1 ppb was given, on the other hand it is produced from the aromatic oxidation by NO and OH.

Partitioning between the phases

Definition of the partition coefficient

Another part of this contribution treated the partitioning of species between the aqueous and gas phase. The partition coefficient ε_{model} was defined as the fraction of species being in the aqueous phase (equation I).

$$\text{I.} \quad \varepsilon_{model} = \frac{c_{aq}^{g}}{c_{aq}^{g} + c_{g}}$$

A special case occurs if species reaches the thermodynamic phase equilibrium so that the partitioning ε_{Henry} between the phases can be predicted by Henry's Law (equation II).

$$\text{II.} \quad \varepsilon_{Henry} = \frac{c_{aq,Henry}}{c_{aq,Henry}^{g} + c_{g,Henry}} = \frac{K_H^{eff}}{K_H^{eff} + 1}$$

c_{aq}^{g} [cm_g^{-3}] = c_{aq} [mol l_{aq}^{-1}] $\cdot N_A \cdot$ LWC (= aqueous phase concentration per cm^3 gas phase)

N_A = Avogadro number ($6.023 \cdot 10^{23}$ mol^{-1})

LWC = liquid water content ($3 \cdot 10^{-10}$ l_{aq} cm_g^{-3})

K_H^{eff} = effective Henry's Law constant (dimensionless)

In the case of acids and aldehydes further dissociation or hydration, respectively, was considered (= effective Henry's Law constant).

All considerations are related to the behaviour of the species as described with the resistance model, meaning that aqueous phase diffusion was not taken into account. So, the values presented here are lower limits for the time scales of partitioning.

$\varepsilon_{model} = \varepsilon_{Henry}$: Hydrogen peroxide

Less reactive species, e.g. hydrogen peroxide, reach the thermodynamic phase equilibrium. The theoretical value for H_2O_2 is $\varepsilon_{Henry} = 0.61$ meaning that 61% of the total H_2O_2 budget in the box are in the aqueous phase. This value is reached after about 30 s after starting the simulation. Observations of the coefficient at longer time scales show that it is constant for the simulation time.

$\varepsilon_{model} > \varepsilon_{Henry}$: Formaldehyde

Another situation exists for formaldehyde being there only to one third unhydrated in the aqueous phase. Its partition coefficient reaches the thermodynamic equilibrium value ($\varepsilon_{Henry} = 0.07$) after about three minutes but after longer times this value is exceeded up to $\varepsilon_{model} = 0.12$. The phase equilibrium shifted to the aqueous phase is constant for the following simulation time of some days. Diagnosis for the sink and source processes shows that formaldehyde is produced very effectively in the aqueous phase from oxidation of methanol by radicals (during day time mainly OH, to a smaller extent Cl_2^-, during night time NO_3). These production processes take place so rapidly that the flux of formaldehyde into the gas phase is too small to adjust this. So for formaldehyde the uptake would be underestimated if it is described only with the effective Henry's Law Constant.

$\varepsilon_{model} < \varepsilon_{Henry}$: Radicals - NO_3 and OH

The NO_3 radical represents the third possible situation between the partition coefficients. Its fraction predicted by the Henry's Law Constant in the aqueous phase amounts only to $\varepsilon_{Henry} = 4.4 \cdot 10^{-6}$ being four orders of magnitude smaller than those of the stable species mentioned above. The value from the model is $\varepsilon_{model} = 4 \cdot 10^{-7}$ being one order of magnitude lower than the theoretical. This is a hint for the high reactivity of the NO_3 radical in aqueous solution: It is consumed so rapidly that even during night time the transport from the gas phase is not fast enough to equalise the loss in the aqueous phase. So it can be summarised that in the case of high reactive species such as the NO_3 radical the uptake is overestimated if it is only described by the Henry's Law.

A combination of all three cases described in the behaviour of the partition coefficient is represented by the OH radical when its partition coefficient is observed over a simulation time of some days. During day time its behaviour can be compared with that of the NO_3 radical during night: In the gas phase a lot of OH is produced (mainly from the reaction between H_2O and O^1D, formed from the ozone photolysis) from which about 50% is transported into the droplet. There it is also consumed rapidly so that the further transport into the droplet is not sufficient. At sunset and sunrise the partitioning of OH is in accordance with the Henry's Law but during night the fraction of OH in the aqueous phase exceeds the value corresponding to the thermodynamic phase equilibrium because it is produced in the aqueous phase from the reactions between FeO^{2+} with H_2O and to a smaller extend by the Fenton reaction. Because in the gas phase there are no effective OH sources during night the equilibrium is shifted then to the aqueous phase.

Conclusion

Effects caused from the update of the aqueous phase mechanism

In the new version of CAPRAM a lot of reactions of the ferryl ion are implemented giving a more detailed description of the chemistry of transition metal ions. This extension reflects mainly the dynamic oxidation and reduction paths for iron.

The importance of the ferryl ion has been shown. Its high reactivity causes a contribution of about 15% to the production of the Fe^{3+} ion. The other main production pathway is the decay of $FeCH_3O_2^{2+}$, formed from the methyl peroxyl radical and Fe^{2+}. These pathways were not considered in the former version of CAPRAM (version 2.3), so that there no dynamic oxidation/ reduction behaviour between the oxidation states of iron could be observed.

In the frame of the revision and update of CAPRAM the C_2 organic chemistry was completed considering now the oxidation of glyoxal, glyoxylic acid and oxalate by radical and radical anions. The oxidation of glyoxal by radicals in the aqueous phase is very effective producing oxalate concentrations in the order of magnitude of 10^{-7} M. Given initial oxalate is oxidised very rapidly to CO_2 by radical and radical anions.

Partitioning

The partition coefficient indicates the fraction of species being in the aqueous phase. It has been shown that stable species such as H_2O_2 reach the thermodynamic phase equilibrium as predicted by the Henry's Law within a time scale of some seconds. Other species such as HCHO are produced in the aqueous phase in large excess so that the transport into the gas phase is too slow to equalise the equilibrium.

The reactivity of radicals (e. g. OH and NO_3) in the aqueous phase is higher than in the gas phase so that their fraction in the droplet is lower than their Henry's solubility. They are consumed immediately after production in the droplet or after the uptake from the gas phase. The inverse behaviour can be observed for OH during night, because there are effective aqueous phase reactions producing OH so that the contribution of aqueous phase processes to the total production flux during night time becomes more important. This leads to a partition coefficient for OH being one order of magnitude higher ($\varepsilon_{model} = 4 \cdot 10^{-3}$) than the value predicted by Henry's Law.

Acknowledgement

The present study is performed within the project 'Model Development for Tropospheric Cloud and Aerosol Chemistry (MODAC)' which is supported by the Commission of the European Communities under contract ENV4-CT97-0388.

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