Size resolved simulation
of a tropospheric multiphase cloud model

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Introduction

The detailed and extended chemical mechanism CAPRAM 2.4 (MODAC mechanism, Chemical Aqueous Phase Radical Mechanism, Model Development for Tropospheric Aerosol and Cloud Chemistry, Herrmann et al., 2000, Ervens et al., 2003, http://www.tropos.de/CHEMIE/multimod/CAPRAM/CAPRAM24.pdf) coupled to the gas phase mechanism RACM (Regional Atmospheric Chemistry Mechanism, Stockwell et al., 1997) was applied to a size-segregated system in order to investigate the influence of size and liquid water distribution on the mass transport processes and on the multiphase chemistry in cloud droplets for three different CAPRAM standard scenarios. Uptake processes of soluble species are included in the mechanism following the approach by Schwartz (1986) considering gas phase diffusion, mass accommodation coefficients, Henry solubility and chemical reaction within the aqueous phase

Model description

The calculations were performed considering a different number of size bins (n=1,2,3,4,5,10,20,30,50) for the particle size range 1µm < $r_{droplet}$ < 64µm assuming a lognormal distribution. For the runs time constant microphysical values were considered. For temperature (T), pressure (p) and the total liquid water content (LWC) the following values were assumed: (T=288 K, p=1 atm and LWC=$3\cdot10^{-7}$ vol_{aq} vol_g^{-1}). The distribution of the number concentration in function of radius is plotted in Figure 1.

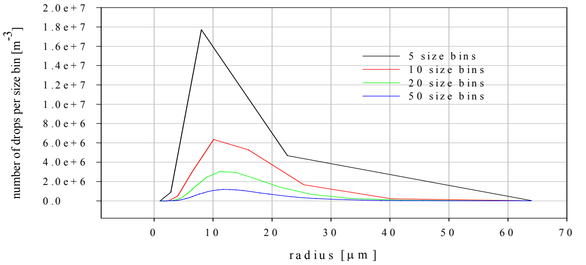

Figure 1: Number of drops per size bin in function of radius for different size resolutions

Results
The iron redox system

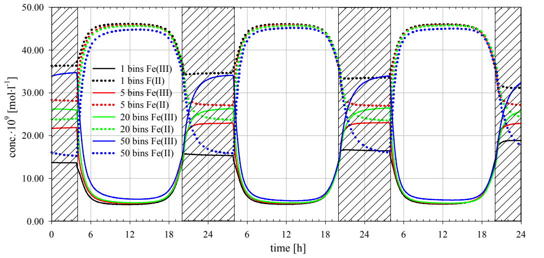

Figure 2: Decreasing [Fe(II)] and increasing [Fe(III)] with a finer droplet spectrum

An interesting size effect can be observed in the case of Fe(III)-Fe(II) especially in the case of marine clouds (Figure 2). Considering different size resolutions the concentrations during the day reach approximately similar values, with the concentration of Fe(II) being higher then the one of Fe(III) at about $4\cdot10^{-8}$ mol·l^{-1}, whereas during the night the concentration of Fe(III) is higher with approximately $2\cdot10^{-8}$ mol·l^{-1} than Fe(II) (considering 50 size bins), but considering only one size bins the concentration of Fe(II) is higher with about $2\cdot10^{-8}$ mol·l^{-1} than the concentration of Fe(III). During the day the following reaction cycle reduces Fe(III) to Fe(II) leading to concentrations of about $4.5\cdot10^{-8}$ mol·l^{-1} and $0.5\cdot10^{-8}$ mol·l^{-1} for Fe(II) and Fe(III), respectively, in all the size bins considered.

$$O_2^- + Fe^{2+} + 2H^+ \rightarrow Fe^{3+} + H_2O_2 \qquad (R1)$$

$$Fe^{3+} + H_2O \rightleftharpoons Fe(OH)^{2+} + H^+ \qquad (R2)$$

$$Fe(OH)^{2+} + H_2O \rightleftharpoons Fe(OH)_2^+ + H^+ \qquad (R3)$$

$$O_2^- + Fe(OH)^{2+} \rightarrow Fe^{2+} + O_2 + OH^- \qquad (R4)$$

$$O_2^- + Fe(OH)_2^+ \rightarrow Fe^{2+} + O_2 + 2OH^- \qquad (R5)$$

During the night the concentration of O_2^- is small. Hence, the oxidation of Fe(II) by H_2O_2 (R6) and by the methyl peroxy radical (R7) become the most important sink processes for Fe(II).

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH + OH^- \qquad (R6)$$

$$CH_3OO\cdot + Fe^{2+} \rightarrow [Fe(CH_3OO)]^{2+} \qquad (R7)$$

While the Fe^{2+} sink processes R6 and R7 are not influenced by size segregation, the reaction cycle R1-R5 is strongly size dependent. The smaller Fe(II) concentration during the night considering a size segregated system can be ascribed to a bigger contribution of R6 and R7 in the big droplets where the concentration of O_2^- is much smaller than in the small droplets. Considering a 1µm radius droplet an O_2^- maximum concentration of about $3.4\cdot10^{-9}$ mol·l^{-1} will occur, while in a 64 µm radius droplet the maximum O_2^- concentration will be about $4\cdot10^{-10}$ mol·l^{-1}. At midnight O_2^- concentrations of about $7.4\cdot10^{-11}$ mol·l^{-1} and $4.4\cdot10^{-12}$ mol·l^{-1} occur in a 1µm and in a 64µm radius droplet, respectively. The difference in the O_2^- concentration is occurring due to differences in the mass transport processes caused by the different surface areas. In the small droplets with big surface area the uptake of HO_2 at midnight represents about 46 % out of the total source of HO_2 in the aqueous phase, while in the big droplets just 1%.

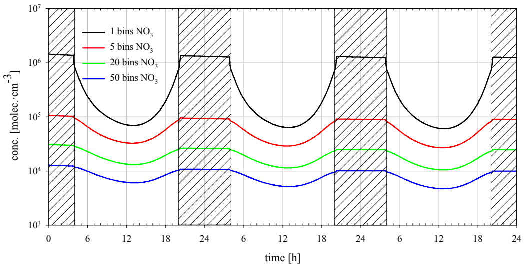

Figure 3: Decreasing NO3 concentration with a finer droplet spectrum (marine scenario)

The nitrate radical

The big difference in the NO_3 concentration considering marine clouds (Figure 3) can be ascribed to phase transfer processes. In a 1µm droplet uptake will represent 37.7 % and 72% at noon and at midnight, respectively, out of the total sink of NO_3 in the gas phase. Uptake into the big droplets (64 µm) encounters just about 0.30 % at noon and 0.57 % at night, respectively. In the urban scenario (Figure 4) contrary to the marine case a finer droplet spectrum leads to a higher NO_3 concentration in the gas phase. The increase in NO_3 concentration is caused by the higher NO_3 concentration in the case of the urban scenario, concentration which is to high to be taken up by the small droplets with small LWC.

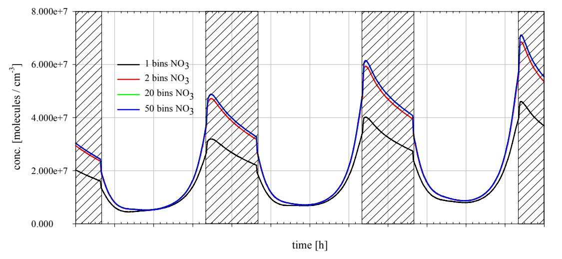

Figure 4: Increasing NO_3 concentration with a finer droplet spectrum (urban scenario)

Overview on size effect on key species

Table 1 contains results obtained for three scenarios, considering a monodisperse distribution (r =10 µm) and a size dependent distribution with 50 different size bins (r =1µm – 64µm). The numbers in Table 1 represent maximum concentrations and are expressed in cm^{-3} for gas phase species and mol·l^{-1} for aqueous phase species.

For most species, the biggest differences between the two distributions are in the case of the marine scenario, due to the stronger contribution of phase transfer processes. In a size segregated system (marine scenario) the OH radical reaches a maximum concentration of about $1.25\cdot10^6$ cm^{-3}, a value considerably smaller than the maximum of a monodisperse system ($2.75\cdot10^6$ cm^{-3}). In the case of N_2O_5 and HONO a difference in concentration of about five orders of magnitude exists between the monodisperse and size segregated case (marine scenario).

gas phase	**Urban**		**remote**		**marine**	
	1 size bins	**50 size bins**	**1 size bins**	**50 size bins**	**1 size bins**	**50 size bins**
O_3	$3.5\cdot10^{12}$	$3.75\cdot10^{12}$	$5.8\cdot10^{11}$	$7\cdot10^{11}$	$6.4\cdot10^{11}$	$5.75\cdot10^{11}$
NO_2	$6\cdot10^{10}$	$5.2\cdot10^{10}$	$8\cdot10^{9}$	$6\cdot10^{9}$	$1\cdot10^{9}$	$1\cdot10^{9}$
NO	$1.35\cdot10^{10}$	$1\cdot10^{10}$	$6\cdot10^{10}$	$4\cdot10^{10}$	$7\cdot10^{8}$	$8.4\cdot10^{8}$
NO_3	$4\cdot10^{7}$	$6\cdot10^{7}$	$4.5\cdot10^{6}$	$7.5\cdot10^{6}$	$1.3\cdot10^{6}$	$1\cdot10^{4}$
OH	$1.75\cdot10^{6}$	$2\cdot10^{6}$	$3.25\cdot10^{6}$	$5\cdot10^{6}$	$2.75\cdot10^{6}$	$1.25\cdot10^{6}$
HONO	$1.8\cdot10^{9}$	$2.65\cdot10^{9}$	$4.7\cdot10^{8}$	$6\cdot10^{8}$	$7\cdot10^{7}$	$1\cdot10^{4}$
N_2O_5	$5\cdot10^{7}$	$2\cdot10^{8}$	$1.75\cdot10^{6}$	$4.5\cdot10^{6}$	$7.5\cdot10^{5}$	$5\cdot10^{0}$
HO_2NO_2	$2.25\cdot10^{9}$	$2.5\cdot10^{9}$	$1\cdot10^{7}$	$3\cdot10^{7}$	$1\cdot10^{6}$	$1\cdot10^{1}$
aqueous phase						
OH	$1\cdot10^{-13}$	$6\cdot10^{-14}$	$2\cdot10^{-13}$	$1.5\cdot10^{-13}$	$5\cdot10^{-13}$	$1.3\cdot10^{-12}$
NO_2	$7\cdot10^{-11}$	$6\cdot10^{-11}$	$8\cdot10^{-12}$	$7\cdot10^{-12}$	$1\cdot10^{-12}$	$1\cdot10^{-12}$
Fe(II)	$1.5\cdot10^{-6}$	$1.5\cdot10^{-6}$	$4.5\cdot10^{-7}$	$4.5\cdot10^{-7}$	$4.5\cdot10^{-8}$	$4.5\cdot10^{-8}$
Fe(III)	$5\cdot10^{-6}$	$5\cdot10^{-6}$	$2\cdot10^{-7}$	$2.5\cdot10^{-7}$	$1.5\cdot10^{-8}$	$3.5\cdot10^{-8}$
Cu^{2+}	$2.5\cdot10^{-7}$	$2.5\cdot10^{-7}$	$5\cdot10^{-8}$	$5\cdot10^{-8}$	$1\cdot10^{-9}$	$1\cdot10^{-9}$
Cu^{+}	$2\cdot10^{-9}$	$1.6\cdot10^{-9}$	$1\cdot10^{-9}$	$1\cdot10^{-9}$	$1\cdot10^{-10}$	$1\cdot10^{-11}$
HO_2	$6.2\cdot10^{-11}$	$4\cdot10^{-11}$	$2\cdot10^{-10}$	$2\cdot10^{-10}$	$2.9\cdot10^{-10}$	$3\cdot10^{-11}$
O_2^-	$1.4\cdot10^{-8}$	$1\cdot10^{-8}$	$7.8\cdot10^{-10}$	$6.4\cdot10^{10}$	$4.5\cdot10^{-9}$	$1.8\cdot10^{-10}$
O_3	$2\cdot10^{-9}$	$2.15\cdot10^{-9}$	$3.4\cdot10^{-9}$	$4\cdot10^{-9}$	$3.5\cdot10^{-10}$	$3\cdot10^{-10}$
HONO	$1.5\cdot10^{-9}$	$2.5\cdot10^{-9}$	$2\cdot10^{-9}$	$2.3\cdot10^{-9}$	$1\cdot10^{-10}$	$5\cdot10^{-14}$
NO_2^-	$1\cdot10^{-10}$	$1.1\cdot10^{-10}$	$7.5\cdot10^{-7}$	$7.5\cdot10^{-7}$	$7.5\cdot10^{-8}$	$5\cdot10^{-11}$
HO_2NO_2	$2.5\cdot10^{-6}$	$2.5\cdot10^{-6}$	$1.075\cdot10^{-9}$	$2.5\cdot10^{-9}$	$5\cdot10^{-10}$	$1\cdot10^{-15}$
Oxalate	$6\cdot10^{-6}$	$5\cdot10^{-6}$	$3.75\cdot10^{-7}$	$2.5\cdot10^{-7}$	$4.75\cdot10^{-7}$	$4\cdot10^{-8}$
HSO_3^-	$7.5\cdot10^{-9}$	$1.1\cdot10^{-8}$	$1\cdot10^{-7}$	$1\cdot10^{-7}$	$1\cdot10^{-8}$	$5\cdot10^{-10}$
SO_3^{2-}	$1\cdot10^{-13}$	$2\cdot10^{-13}$	$8\cdot10^{-9}$	$8\cdot10^{-9}$	$1\cdot10^{-9}$	$5\cdot10^{-11}$

Table 1: Resulted maximum concentrations considering a monodisperse and a size segregated system with 50 size bins

Summary and Conclusion

The detailed and extended chemical mechanism CAPRAM 2.4 (MODAC mechanism) was applied to a size resolved system considering different number of size bins. In the present work up to 50 different size bins were considered with a radius between 1µm and 64 µm. The results showed that size segregation has a great effect on phase transfer processes and subsequently on diurnal concentration profiles. The biggest changes are encountered in the case of the marine scenario due to the bigger contribution of phase transfer processes.

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