Concentration Profiles Using a Lognormal Distribution Regarding Aerosols with CAPRAM 2.4 (MODAC Mechanism)

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Introduction

CAPRAM 2.4 (Chemical Aqueous Phase Radical Mechanism) (Herrmann *et al.*, 2002) is a detailed and extended chemical mechanism describing tropospheric aqueous phase chemistry (147 species 438 reactions). The model was applied to a size-segregated system in order to investigate the influence of size distribution and liquid water distribution on the mass transport processes and on the multiphase chemistry in cloud droplets for three different scenarios. The aqueous chemistry has been coupled to the gas phase mechanism RACM (Stockwell *et al.*, 1997) and phase exchange accounted by the resistance model of Schwartz (Schwartz, 1986).

Model description

The calculations were performed with a 0-dimensional box model considering different number of size bins (1,2,3,4,5,10,20,30,50) ($1\mu m < r_{droplet} < 64\ \mu m$). For the runs time constant microphysical values (liquid water content, no liquid water fluxes between different droplet classes) 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=$3 \cdot 10^{-7}$ $vol_{aq}\ vol_g^{-1}$). The distribution of the number concentration in function of radius is plotted in Figure 1.

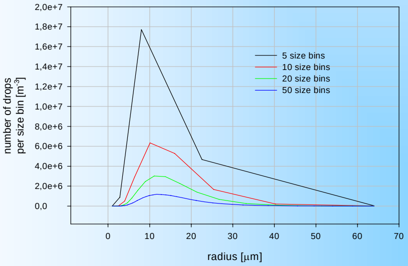

Figure 1: Number of drops per size bin in function of radius for different size resolutions

Results

The iron redox sytem

An interesting size effect can be observed in the case of Fe(III)-Fe(II), especially in the remote and marine cases (Figure 2). While considering different size resolutions the concentrations during the day reach approximately similar values,, with the concentration of Fe(II) being higher then that one of Fe(III) by approx. $4 \cdot 10^{-8}$ mol/l during the night the concentration of Fe(III) will be higher with approx. $2 \cdot 10^{-8}$ mol/l than Fe(II) (considering 50 size bins), but considering only one size bins the concentration of Fe(II) will be over Fe(III) by approx. $2 \cdot 10^{-8}$ mol/l. (marine scenario) According to our simulations, considering urban clouds Fe(II) is peaking around eight o clock in the morning, when also Fe(III) has a minimum. Investigations were carried out to explain this behaviour. The most important sources for Fe^{2+} are the reactions of Fe^{3+} or $FeOH^{2+}$ with Cu^+. This source processes have a maximum around 8 A.M. reaching values about $1.5 \cdot 10^{-7}$ respectively $1.25 \cdot 10^{-7}$ $mol \cdot l^{-1} \cdot s^{-1}$.The most important sink for Fe^{2+} is the reaction with HO_2 reaching a maximum of $2.5 \cdot 10^{-7}$ around 8 a.m. Investigating the sinks and sources of Cu^+ it becomes evident that the most important source is the reduction of Cu^{2+} by HO_2. This process reaches a maximum of about $1.5 \cdot 10^{-5}$ around 12 a.m. As a conclusion, at the beginning of the day HO_2 concentration is increasing, reducing Cu^{2+}, witch yields Cu^+ witch is reducing Fe^{3+} How the concentration of HO_2 is getting bigger and bigger, the reaction $HO_2 + Fe^{2+}$ will be more and more important, yielding a maximum concentration for Fe^{2+} around eight o clock in the morning.

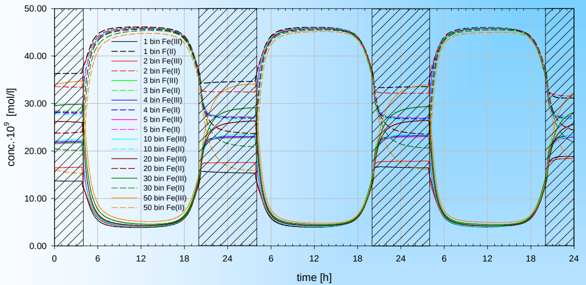

Figure 2: Size effect during the night in the iron redox system

Radical chemistry in the gas phase

At the first look the results for the OH radical seems contradictory. Considering marine clouds (Figure 3), and multiple size bins the concentration will be lover than in the case of one size bins reaching a value of approx. $1.5 \cdot 10^6$ cm^{-1} instead of $2.75 \cdot 10^6$ cm^{-1}.In the case of polluted urban clouds (Figure 4) the size effect is much smaller, considering multiple size bins the concentration being higher with approx. $0.25 \cdot 10^6$ cm^{-1} The explanation would be that size resolution affects primordially uptake processes. The contribution of the phase transfer processes is much more important in the case of marine scenario representing 2.7 % of the total sink at noon and 82 % of the total source at midnight. In the case of urban clouds phase transfer represents only 0.2 % out of the total sink at noon and 0.1 % from the total sink at midnight. The same behaviour can be observed in the case of NO_3 when considering multiple size bins the concentration will raise in the urban scenario but will decrease in the marine scenario compared to the results obtained with only one size bins.

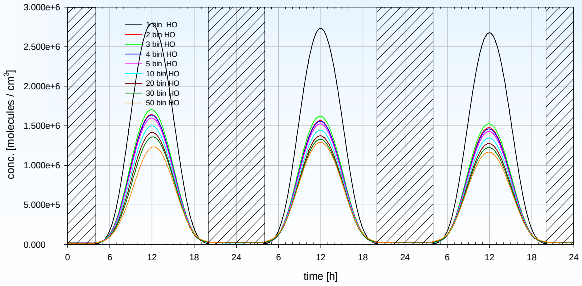

Figure 3: OH concentration over the simulation time (marine scenario)

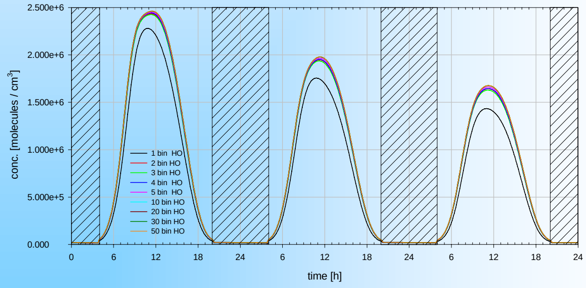

Figure 4: OH concentration over the simulation time (urban scenario)

Overview on size effect on key species

Table 1 contains the results obtained with 1 respectively 50 size bins. The concentrations in the gas phase are expressed in cm^{-3} and in $mol \cdot l^{-1}$ for the aqueous phase. The values represents maximum concentrations. It can be seen that the biggest changes will occur in the case of marine clouds. Another observation would be that in the marine scenario some species are not affected by the size resolution In these cases the concentration in both phases will not be affected. These observations led us to the conclusion that phase transfer is primordially affected by size resolution, process witch is most important in marine conditions.

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

Summary and Conclusion

According to the results, it becomes evident that size resolution has a great effect on concentration. It can be concluded that size effect is more important in the case of marine clouds, than in the case of urban conditions, due to the bigger contribution of phase transfer processes.

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