CAPRAM MODELLING OF THE SPECIATION AND REDOX-CYCLING OF IRON IN DELIQUESCENT PARTICLES AND CLOUD DROPLETS

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Introduction and Model Outline

The most abundant transitional metal ion (TMI) in tropospheric particles is iron which plays a crucial role in aqueous phase chemistry of fog and cloud droplets (Deguillaume et al. [2005]). The redox-cycling of iron is responsible for many chemical interactions such as the HO_x/HO_y processing. However, still large uncertainties about the TMI chemistry exist. To this end, the iron speciation and redox-cycling in deliquescent particles and cloud droplets have been investigated in more detail by means of model studies using the SPectral Aerosol Cloud Chemistry Interaction Model (SPACCIM, Wolke et al. [2005]). The model studies were particularly focused on temporal variations in the of iron speciation and redox-cycling in the condensed phase including its importance for other important chemical subsystems such as the multiphase HO_x/HO_y and organic chemistry. For this purpose, sensitivity studies were performed on the importance of the water soluble iron content for the aqueous phase oxidation capacity and the organic chemical processing.
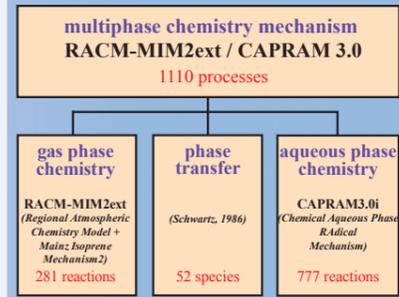
multiphase chemistry mechanism
RACM-MIM2ext / CAPRAM 3.0
1110 processes

gas phase chemistry	phase transfer	aqueous phase chemistry
RACM-MIM2ext		**CAPRAM3.0i**
(Regional Atmospheric Chemistry Model + Mainz Isoprene Mechanism2)	*(Schwartz, 1986)*	*(Chemical Aqueous Phase RAdical Mechanism)*
281 reactions	52 species	777 reactions

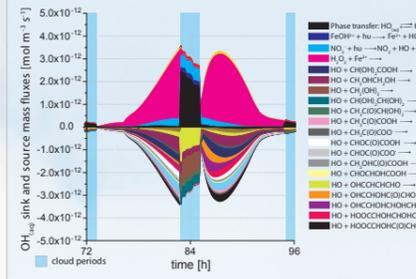*Figure 1:* Schematic representation of the applied multiphase chemistry mechanism.

Table 1: Overview on the characteristics of the sensitivity cases (Fe1 represents the "primary scenario").

Sensitivity case	Scaling factor	Water soluble iron content
Fe1	$^1/_1$ (100 %)	10 %
Fe2	$^1/_4$ (25 %)	2.5 %
Fe3	$^1/_{16}$(6.25 %)	0.625 %
Fe4	$^1/_{64}$(1.56%)	0.0156 %

The parcel model SPACCIM includes a complex microphysical and multiphase chemistry model which allows a detailed description of the processing of gases, deliquescent particles and cloud droplets. For the multiphase chemistry description, the RACM-MIM2ext/CAPRAM 3.0i mechanism (Karl et al. [2006], Herrmann et al. [2005]) with about 1110 processes was applied incorporating a detailed description of the TMI chemistry. The chemical model was initialised with physical and chemical data from the EUROTRAC-2 project CMD (Poppe et al. [2001] and references therein). For the simulations a finely resolved particle spectrum is considered. Simulations were carried out for different environmental conditions using a non-permanent meteorological cloud scenario which were derived from the global calculations of Pruppacher and Jaenicke [1995]. In the model scenario, an air parcel moves along a predefined trajectory including 8 cloud passages of about 2 hours within 108 hours modelling time and an intermediate aerosol state at a 90 % relative humidity level by neglecting the effects of non-ideal solutions. The model results have been analysed including time-resolved source and sinks reaction flux studies.

The sensitivity studies have been performed for the urban scenario due to the more effective redox-cycling under polluted conditions. For the sensitivity studies, the initialised water-soluble iron fraction of the base case ("primary scenario" referred to as Fe1) has been scaled by $^1/_4$ (Fe2), $^1/_{16}$ (Fe3) and $^1/_{64}$ (Fe4), respectively (see *Table 1*). The studies have been particularly focused on the HO_x/HO_y budget effects and its feedback on the multiphase organic C_2 chemistry.

Model Results

Iron speciation in deliquescent particles and clouds

The iron speciation is an indicator for the atmospheric oxidation and reduction potential as well as the reactivity of the aqueous phase radical chemistry.

- $\delta([Fe(II)])$ ratios show a characteristic diurnal profile for both scenarios (good agreement to several field studies)
- Obtained patterns reflect the dynamic time-dependent iron redox-cycling in both cloud droplets and deliquescent particles
- Diurnal cycling more noticeable under urban conditions caused by the more efficient iron processing under high HO_x/HO_y conditions in the particle phase (relatively small differences between cloud and aerosol conditions under polluted conditions)
- At noon (midnight), approximately 80 % (40 %) and 80 % (50 %) of the total soluble iron exists in its oxidation state +II in the urban and remote clouds, respectively (Fe(II) exists almost completely as Fe^{2+} in clouds and aqueous particles)
- Fe(III) fraction consist mainly of Fe(III) oxalate complexes ($[Fe(C_2O_4)]^+$ and $[Fe(C_2O_4)_2]^-$) and the iron-sulphato-complex $[Fe(SO_4)]^+$ in the deliquescent particles under both urban and remote conditions (see *Table 2*).
- Iron-hydroxo-complexes ($Fe(OH)_2^+$ and $FeOH^{2+}$) contribute on an average of 12 % and 46 % considerably to the total Fe(III) budget only in urban and remote clouds (due much lower pH values under aqueous particle conditions).
- Modelled contributions of the iron-oxalato-complexes are presumably underestimated because of the underpredicted oxalate budget
- During night about 20 to 50 % of the soluble iron (average: 34 %) still present as Fe^{2+} reflecting an efficient nighttime iron-redox-cycling
- Better agreement with the observations than former model studies of Ervens et al. [2003] and Deguillaume et al. [2004] (nighttime cloud water measurements of the Fe(II) content found values between 20 % and 60 % (see Deguillaume et al. [2005])

$$\delta([Fe(II)]) = \frac{[Fe(II)]}{[Fe(II)]+[Fe(III)]}$$
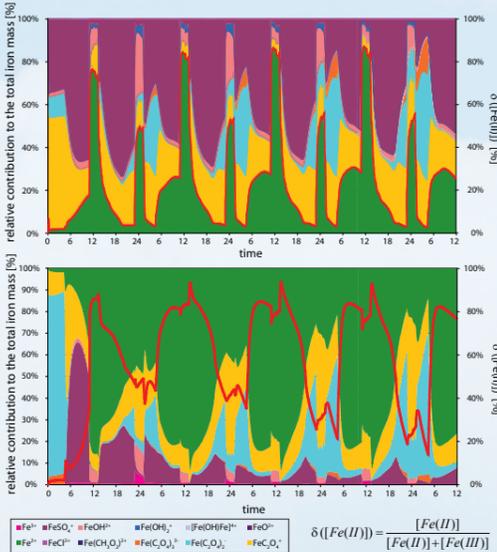
Figure 2: Temporal evolution of the relative contributions [%] of different iron species to the total iron mass under remote (top) and urban (down) environmental conditions. The red line shows the percentage contribution of Fe(II) species to the total iron content.

Table 2: Mean percentage contributions of the main Fe(III) compounds to the total Fe(III) in cloud droplets (CD) and aqueous particles (AP) for the urban and remote case.

Species	Urban case		Remote case	
	CD	AP	CD	AP
Fe $^{3+}$	3.8%	1.2%	2.1%	1.1%
$FeSO_4^+$	2.4%	26.2%	7.2%	54.7%
$FeOH^{2+}$	11.9%	0.4%	38.2%	2.8%
$Fe(OH)_2^+$	0.2%	0.0%	8.1%	0.1%
$FeCl^{2+}$	0.0%	0.0%	0.0%	0.1%
$Fe(C_2O_4)^+$	67.9%	34.1%	31.2%	28.3%
$Fe(C_2O_4)_2^-$	13.6%	36.8%	12.9%	11.6%
$Fe(C_2O_4)_3^{3-}$	0.1%	1.3%	0.2%	1.4%

Phtochemical iron(II) cycling

- Iron (II) sink and source reaction fluxes show a characteristic daytime profile which is perturbed by the cloud periods
- Total daytime fluxes in the deliquescent particles are partly about 2 times larger than in daytime clouds
- Iron redox cycling is potentially more efficient in the aqueous particles than in clouds under urban conditions

Table 3: Integrated percentage contributions of the most important Fe(III) sources and sink reactions under urban aqueous particle and cloud conditions.

Reaction	Total	Cloud droplets	Aqueous particles
$Fe^{3+} + Cu^+ \longrightarrow Fe^{2+} + Cu^{2+}$	-69.2%	-26.7%	-75.1%
$H_2O_2 + Fe^{2+} \longrightarrow Fe^{3+} + OH + OH^-$	41.0%	6.6%	45.7%
$HO_2 + Fe^{2+} (+ H_2O) \longrightarrow Fe^{3+} + H_2O_2 + OH^-$	22.4%	36.9%	20.4%
$FeOH^{2+} + Cu^+ \longrightarrow Fe^{2+} + Cu^{2+} + OH^-$	-16.8%	-28.9%	-15.1%
$FeO^{2+} + Fe^{2+} (+ H_2O) \longrightarrow 2 Fe^{3+} + 2 OH^-$	15.9%	12.0%	16.5%
$Fe(C_2O_4)_2^- + hv \longrightarrow Fe^{2+} + C_2O_4^{2-} + CO_2 + CO_2^-$	-7.5%	-1.3%	-8.4%
$OH + Fe^{2+} \longrightarrow FeOH^{2+}$	4.7%	1.2%	5.2%
$FeO_2H_2^{2+} + H^+ \longrightarrow Fe^{3+} + CH_3OOH$	4.7%	3.3%	4.8%
$O_2^- + FeO^{2+} \longrightarrow Fe^{3+} + O_2 + OH^-$	-3.6%	-28.0%	-0.2%
$Fe^{2+} + SO_4^- (+ H_2O) \longrightarrow FeOH^{2+} + SO_4^{2-} + H^+$	2.7%	3.6%	2.6%
$O_2^- + Fe^{2+} (+2 H^+) \longrightarrow Fe^{3+} + H_2O_2$	2.2%	15.8%	0.4%
$Fe(OH)_2Fe^{4+} \longrightarrow 2 Fe^{3+} + 2 OH^-$	1.2%	0.9%	1.2%
$HSO_5^- + Fe^{2+} \longrightarrow SO_4^- + FeOH^{2+}$	1.1%	8.5%	0.1%
$FeOH^{2+} + hv \longrightarrow Fe^{2+} + OH$	-1.0%	-7.1%	-0.2%
$FeO^{2+} + Fe^{2+} \longrightarrow Fe(OH)_2Fe^{4+} + H_2O$	0.8%	0.5%	0.8%
$FeCH_3O_2^{2+} \longrightarrow Fe^{3+} + CH_3OOH + OH^-$	0.7%	2.9%	0.4%
$Fe(OH)_2Fe^{4+} (+ H^+) \longrightarrow 2 Fe^{2+} + OH + H_2O$	-0.6%	-0.5%	-0.6%
$FeO^{2+} + HCOO^- (+ H^+) \longrightarrow Fe^{3+} + CO_2H + OH^-$	0.6%	4.5%	0.0%
$O_2^- + Fe^{3+} \longrightarrow Fe^{2+} + O_2$	-0.5%	-3.9%	0.0%
Total sources	98.0%	96.7%	98.1%
Total sinks	-99.2%	-96.4%	-99.6%

Figure 3: Depiction of the modelled aqueous phase chemical sink and source mass fluxes of Fe(II) in mol m⁻³ s⁻¹ for a selected period of the modelling time (third model day) under urban conditions.

- Chemical differences in the sink and source reactions between aqueous aerosol and cloud conditions (caused by different pH conditions as well as the different HO_2/O_2^- budget in the two aqueous environments)
- Most important sources of Fe(III) in the aqueous phase under urban cloud conditions are reactions of Fe^{2+} with HO_2/O_2^- with about 37% and 16% (1% and 53% in the remote case)
- Fe(III) formation in the deliquescent particles dominated by the Fenton reaction with contributions of about 60 % and 46 % in the remote and urban case, respectively
- Photolytic decomposition of iron-organo-complexes potential source for the radical budget in deliquescent particles?

Importance of the iron-redox-cycling

- OH formation dominated by the Fenton reaction of Fe(II) with H_2O_2 in the deliquescent particles (in-situ OH production)
→ direct correlation between the photochemical formation of OH in deliquescent particles and the dissolved iron also found in sampled aqueous particle extracts (Arakaki et al. [2006])
- Total source fluxes in the aqueous particles are fully comparable with that in the cloud droplets under urban conditions
→ implication of the potential relevance of deliquescent particles to act as a reactive medium within the tropospheric multiphase system (particularly entrainment and detrainment areas of clouds maybe quite reactive media for the chemical aerosol processing)
- Daytime cloud chemistry can act as source of H_2O_2 due to an effective TMI-chemistry (interaction of iron and copper with HO_2/O_2^-)
→ direct chemical cloud effect
→ compensation of the sulfur oxidation pathway
→ feedback on the gas phase HO_x/HO_y budget

Figure 4: Chemical flux analysis of the main aqueous phase sink and source processes of the OH radical in mol m⁻³ s⁻¹ for urban conditions (top) and modelled gas phase concentrations of H_2O_2 for remote conditions.

Current mechanisms which include the formation and photolytic decay of iron-oxalate-complexes are currently not able to reproduced observed oxalate concentrations levels and diurnal concentration profiles in the field. Even under polluted conditions with a huge input flux from the oxalate precursors, the daytime produced oxalate is quickly consumed by the photolysis (see *Figure 5*). Therefore, the modelled urban concentrations are about 10 times smaller than typically observed oxalic acid levels in heavily polluted environments. This dilemma could be caused by both an underestimation of the oxalate productions (missing organic chemistry input from other higher organic oxidation paths, which are currently not considered in CAPRAM) and an overestimation of its degradation (primarily the photolytic decay of its iron-complexes) in the current model. The CAPRAM mechanism neglects maybe currently other photochemical active substances such as chromophoric humic like compounds as well as other efficient organic ligands for the iron complexation. Those compounds are also able to photodegradate efficiently under ambient radiation conditions and can act as competitive photolytic sinks. Thus, the model overestimates probably the photolytic iron-oxalate-complex decay.
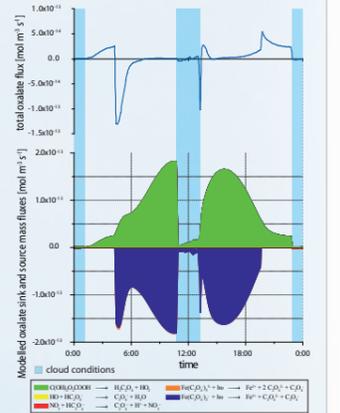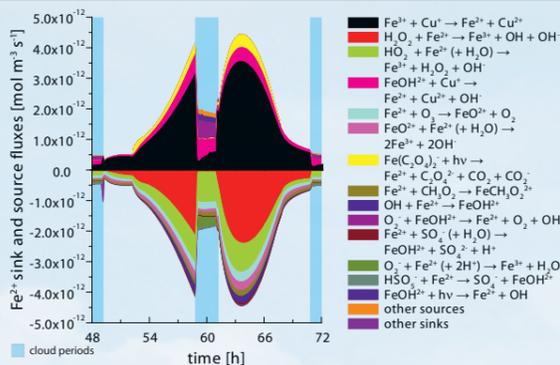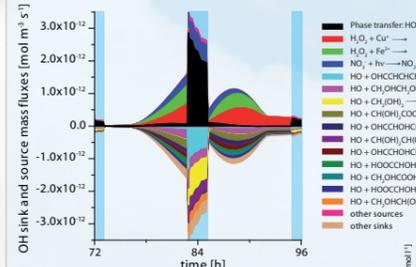
Figure 5: Depiction of the modelled aqueous phase chemical sink and source mass fluxes of oxalic acid/ oxalate in mol m⁻³ s⁻¹ for the second model day under urban conditions.

Sensitivity studies on the importance of the water-soluble iron content

- Sensitivity studies show significant effects of the soluble iron content predominantly on the aqueous phase HO_x/HO_y budget
- reductions of the aqueous OH radical budget noticeable particularly under deliquescent particle daytime conditions (modelled concentrations in the Fe3 case about 75 % smaller (after 64 h) compared to the base case Fe1)
- Considerable decreases of both source and sink fluxes under deliquescent particle conditions (cp. *Figure 6*; Fe3 flux about 50 % smaller than respective flux in the Fe1 case) and changed source flux pattern

Figure 6: Modelled chemical sink and source mass fluxes of OH in aqueous phase mol m⁻³ s⁻¹ for the fourth day of modelling time for the urban scenario (Fe3).

- Multiphase H_2O_2 budget by far less reduced with decreasing water-soluble iron content (less effective Fenton chemistry)
- Less efficient iron chemistry and the higher H_2O_2 concentrations cause an increase in the efficiency of other oxidation processes such as the S(IV) to S(VI) conversion.
→ indirect effect of the iron redox chemistry leads to approximately 20 % higher S(VI) concentrations in Fe4 at the end of the simulation time compared to the Fe1 case
- Due to the reduced OH formation in the deliquescent particles, OH-driven oxidations are consequentially decreased
→ higher concentrations and longer lifetimes of organic cloud chemistry oxidation products such as glyoxalic acid (see *Figure 7*) .
- For oxalic acid the reduced available iron leads to a decreased iron-oxalate-complex formation and photolytic decay of the organic complexes
→ more realistic urban concentration of oxalate can be modelled (dilemma of present modelling concerning the iron-oxalate photolysis, see above)

Figure 7: Modelled urban $OH_{(aq)}$, $HO_{2(aq)}/O_2^-$, $H_2O_{2(gas)}$, total sulphur(VI), glyoxalic acid and oxalic acid concentrations as a function of the simulation time modelled with different water-soluble iron contents.

Summary and Outlook

Simulations with the parcel model SPACCIM have been carried out for different atmospheric conditions to investigate the iron speciation and redox-cycling in deliquescent particles and cloud droplets. Furthermore, the importance of the water soluble iron content for the aqueous phase oxidation capacity and the organic chemical processing have been investigated by means of sensitivity studies. The model results have pointed out considerable chemical differences between the iron processing in deliquescent particles and cloud droplets. Moreover, the studies revealed a circa two times more efficient daytime iron processing in the particle phase which implicates the potential role of deliquescent particles to be a reactive medium for the TMI redox-cycling and for other associated chemical subsystems. Performed comparisons with available cloud water measurements revealed both reasonable agreements and differences. The performed studies regarding the relevance of the water-soluble iron content for tropospheric multiphase processes have pointed out that the oxidation budget is quite sensitive to changes of this crucial parameter. Accordingly, the sensitivity studies corroborate the need for an iron-redox-chemistry treatment in higher scale chemistry transport models.
In conclusion, the performed model studies have provided a deeper insight into the diurnal iron speciation and processing in cloud droplets and aqueous particles. However,the studies have also confirmed that a precise modelling of the iron speciation and comparison with field data is still rather complicated and needs further laboratory and field investigations and subsequent aqueous phase mechanism enhancements. Particularly, further experimental work concerning the iron organic aqueous photochemical interactions is necessary to clarify open scientific issues and mechanism limitations.

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