

## Introduction and Motivation

Recent detailed 0-D multiphase chemistry model studies [e.g. Tilgner and Herrmann, 2009] have implicated the necessity of more complex aqueous phase processes to be considered in future higher scale chemistry transport models (CTMs). Important chemical cloud effects are mainly not yet considered or less represented in currently available regional scale CTMs because of both the restricted knowledge in the past and the high computational costs of detailed aqueous phase chemistry mechanisms such as CAPRAM 3.0i (Chemical Aqueous Phase RAdical Mechanism, Tilgner and Herrmann [2009]). In this context, mechanism reductions using manual methods and automatic techniques have been already carried out to develop simplified chemical mechanisms. First objective of the present work was to develop a reduced aqueous phase CAPRAM mechanism which is operational in higher scale CTMs. The mechanism reduction was aimed to develop a chemical mechanism with a manageable size (about 250 chemical processes) which accurately represents the main chemical processes viz. without a loss of key information. This will allow further investigations of the multiphase chemical processes for a wider range of conditions in shorter time periods and in higher scales together with transport and microphysical processes in future regional CTMs. Second objective of the present work was to examine the applicability of the reduced mechanism for later regional scale applications by means of 2D test simulations with the MUSCAT model [Wolke et al., 2004].

The mechanism reduction has been performed by means of a manual method including detailed chemical flux investigations and an automatic method. Both methods have been focused on the identification and depletion of less important chemical processes to provide a less computationally intensive mechanism. Finally, the results of the two reductions have been compared. Based on the limitations of both reduction methods, the reduced CAPRAM mechanism was finally derived.

For the automatic reduction (AR), the ISSA-method (Iterative Screening and Structure Analysis, Mauersberger [2005]) was used to determine unimportant chemical processes and species in CAPRAM 3.0i mechanism. The reduction has been done by G. Mauersberger in the same manner as presented in Mauersberger [2005] for the former CAPRAM version 2.4 using a permanent cloud model scenario. The manual reduction (MR) was performed similarly to the studies of Ervens et al. [2003] based on detailed chemical flux analyses for pre-selected key species and was mainly focused on the organic chemistry. The MR reduction studies have been carried out with the SPectral Aerosol Cloud Chemistry Interaction Model (SPACCIM, Wolke et al. [2005]). In this parcel model, a non-permanent meteorological cloud scenario was applied including an extended cloud passage of about 26 hours within 48 hours modelling time. The target species have been chosen relative to their roles in tropospheric chemistry. For the identification of important reaction paths and species, detailed chemical flux analyses have been performed mainly for the target species in different atmospheric scenarios.

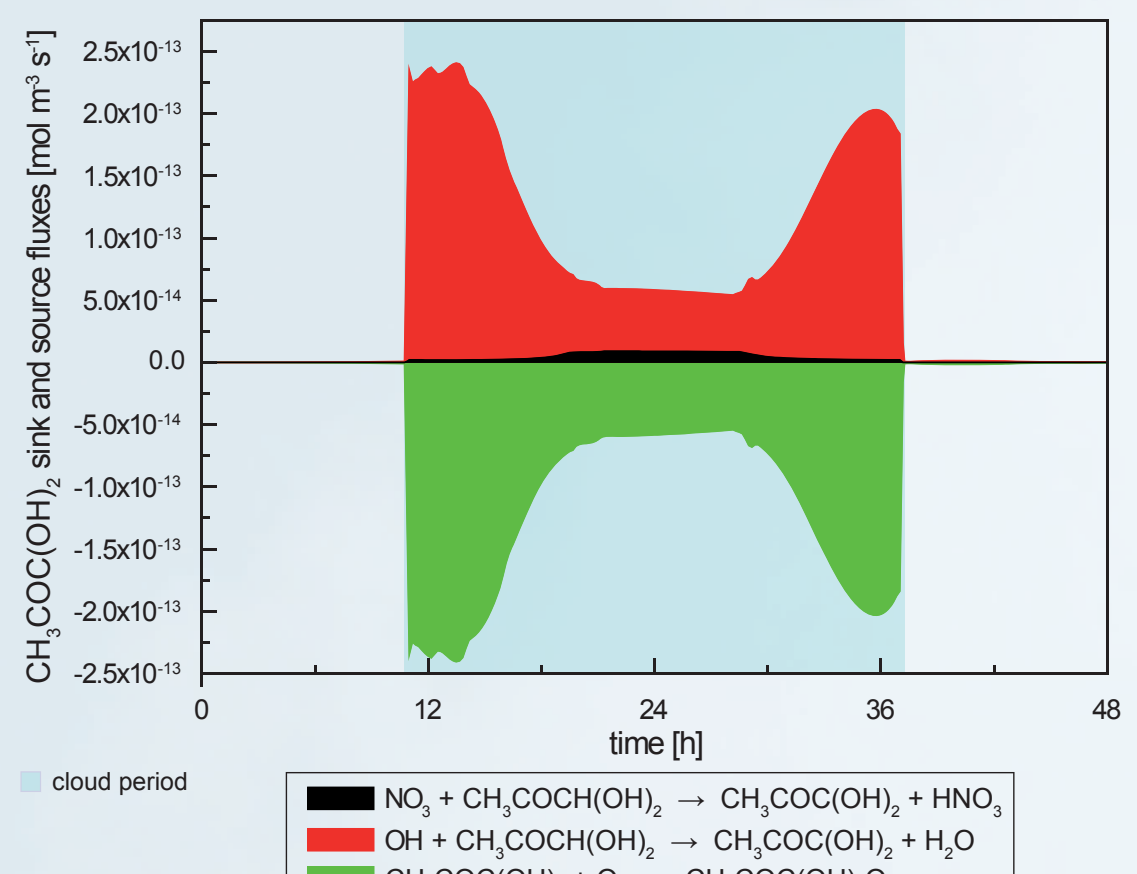


## Mechanism Reduction

### • Detection of reaction rate-determining steps in the reaction chains of the organic chemistry (MR)

The studies have shown that for the majority of the organic oxidations the peroxy radical formation and the uni- or bi-molecular  $\text{RO}_2$  decomposition are not reaction rate-determining steps. Consequently, these processes were deleted and the linear step by step reaction pathways were linked together by reducing the number of reaction steps and species considering only the rate limiting reaction steps which are mostly only the initial radical reactions.

Figure 1: Modelled sink and source fluxes of the hydrated 2-oxo propionyl radical [ $\text{CH}_3\text{C}(\text{O})\text{C}(\text{OH})_2$ ] for remote conditions.



### • Chemical analysis of important aqueous phase chemical subsystems and reductions (MR)

- Deletion of effective hydrate formation processes and hydroxy methane sulfonate oxidation scheme
- Simplification of the sulphur radical subsystem
- Reduction of less important  $\text{NO}_3$  radical oxidations of organic compounds (see Figure 2) and the aqueous chemical processing of organic acids such as acetic, propanoic and butyric acid (see Figure 3)

### • Deletion of less important organic subsystems (MR, see Figure 3)

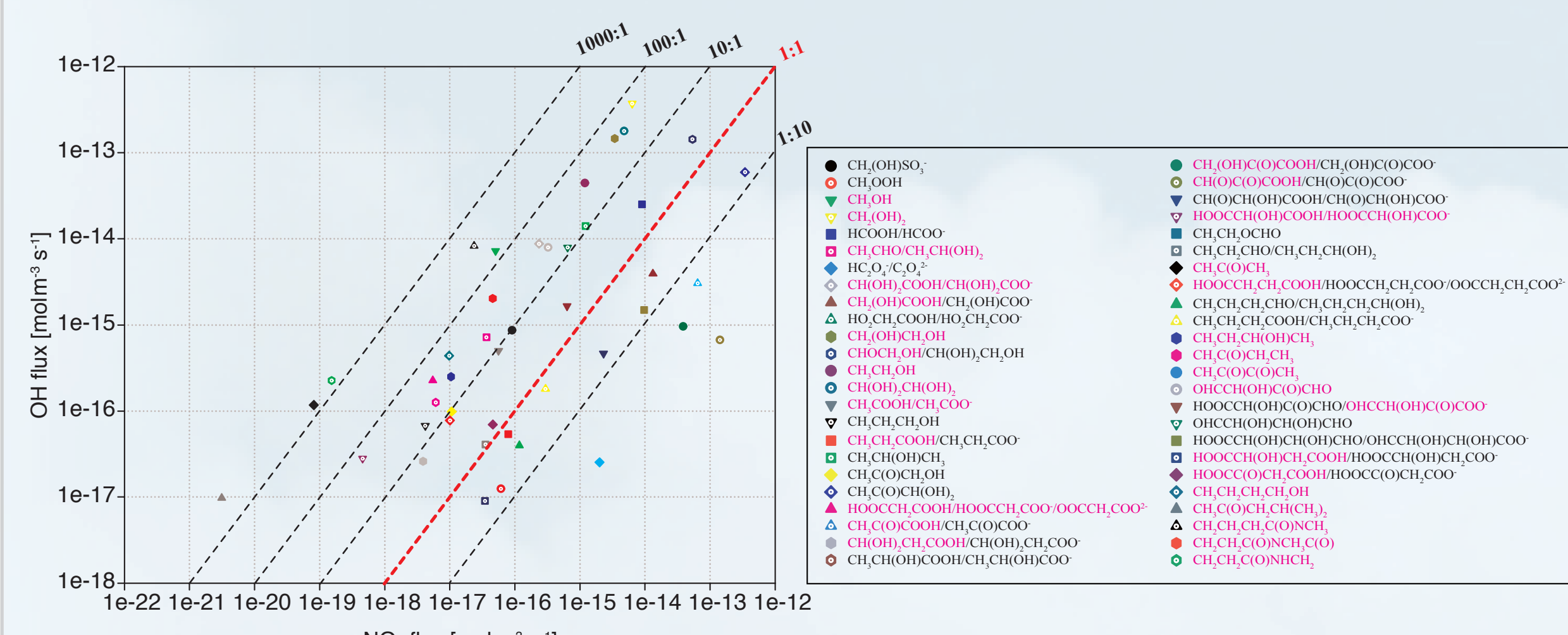


Figure 2: Comparison of the mean modelled in-cloud  $\text{NO}_3$  and OH degradation fluxes of organic compounds under urban conditions. For magenta-marked chemical compounds the percentage contribution of the  $\text{NO}_3$  reaction to their total degradation is less than 5%. These  $\text{NO}_3$  oxidations were removed from the mechanism.

### • Comparison of the AR and MR results

Comparison of the manual and automatic reduction shows a good agreement with minor differences in the organic chemistry. Inorganic chemical mechanism part was almost the same than obtained in previous reduction studies (Mauersberger [2005]). Based on the limitations of used methods a postprocessing of generated mechanisms was done to merge the reduction results and to derive adequate and feasible reduced mechanism. Based on the obtained mechanism differences, the inorganic chemical processes in the final reduced mechanism have been mainly considered according to the AR results and the organic chemistry is implemented in the final mechanism (C3.0RED) following the manual reduction results (including the lumping and reformulation of the oxidation chains).

Aqueous phase mechanism	C3.0	C3.0RED
Number of aqueous reactions	676	138
Number of photolysis reactions	12	5
Mass transfer processes	51	41
Equilibria	89	55
Total number of chemical processes	777	198
Number of aqueous species	380	130

- Percentage deviations between the two mechanisms are mostly below 5% for most of the target species (see Table 2)
- Reduction of the total required CPU time by approximately 40% (see Figure 5)

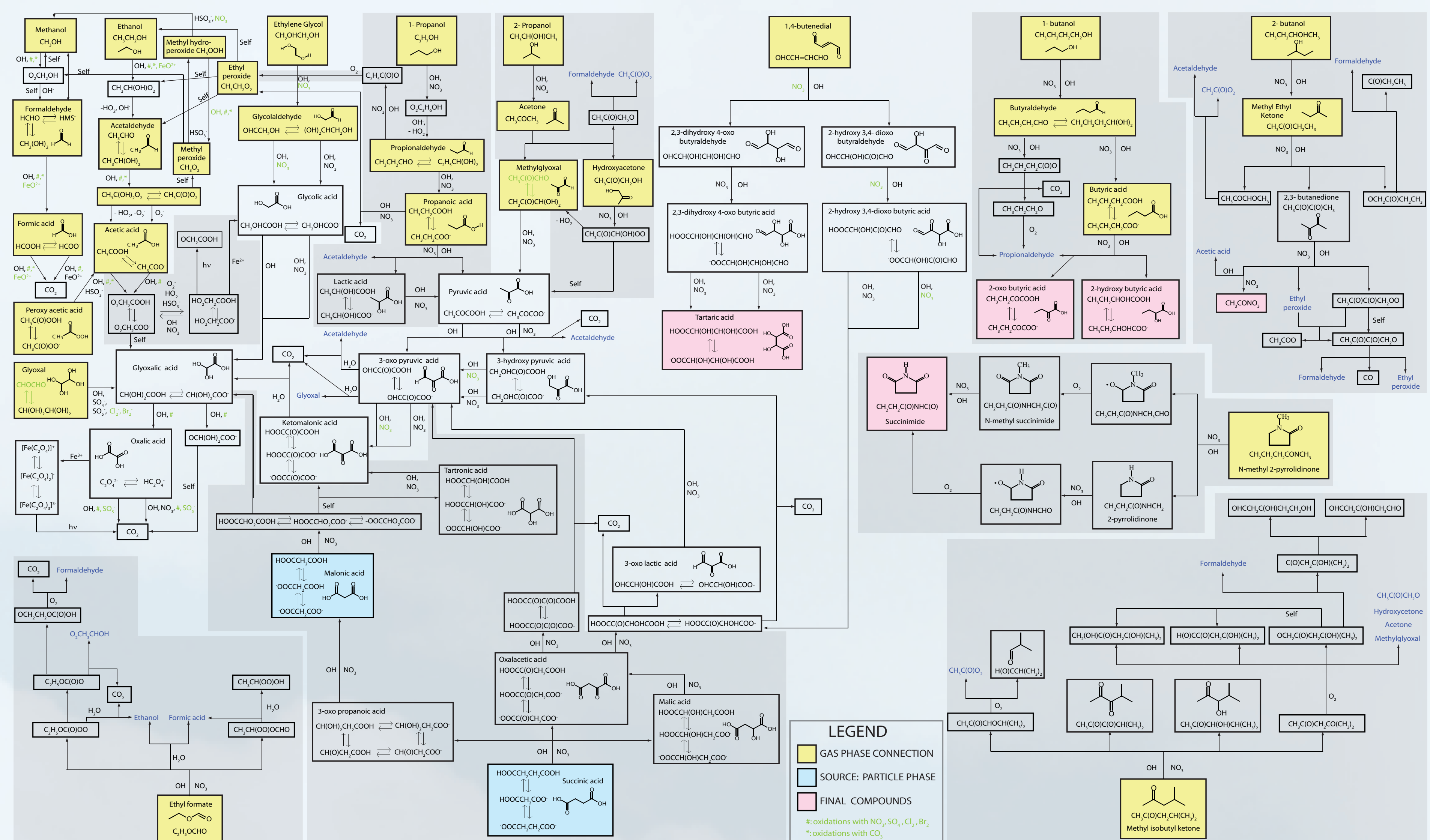


Figure 3: Schematic depiction of the organic chemistry in C3.0RED. The reduced chemical organic subsystems compared to the full CAPRAM 3.0i mechanism are indicated by a grey background and marked in green. (For purpose of clarity, the explicit oxidation scheme of the full aqueous phase mechanism including peroxy radical formation and recombination reactions is not displayed as far as these processes are not considered in the reduced mechanism.)

C3.0RED		C3.0	
Total number of processes:			
HO <sub>x</sub> / TMI	198	777	
Nitrogen	7	32	
Sulphur	19	59	
Bromine	2	17	
Chlorine	6	16	
Organics (C1-C4)	74	472	
Carbonate	0	21	
Equilibria	55	89	
Photolysis	5	12	

Figure 4: Comparison of the full and the reduced CAPRAM3.0i mechanism.

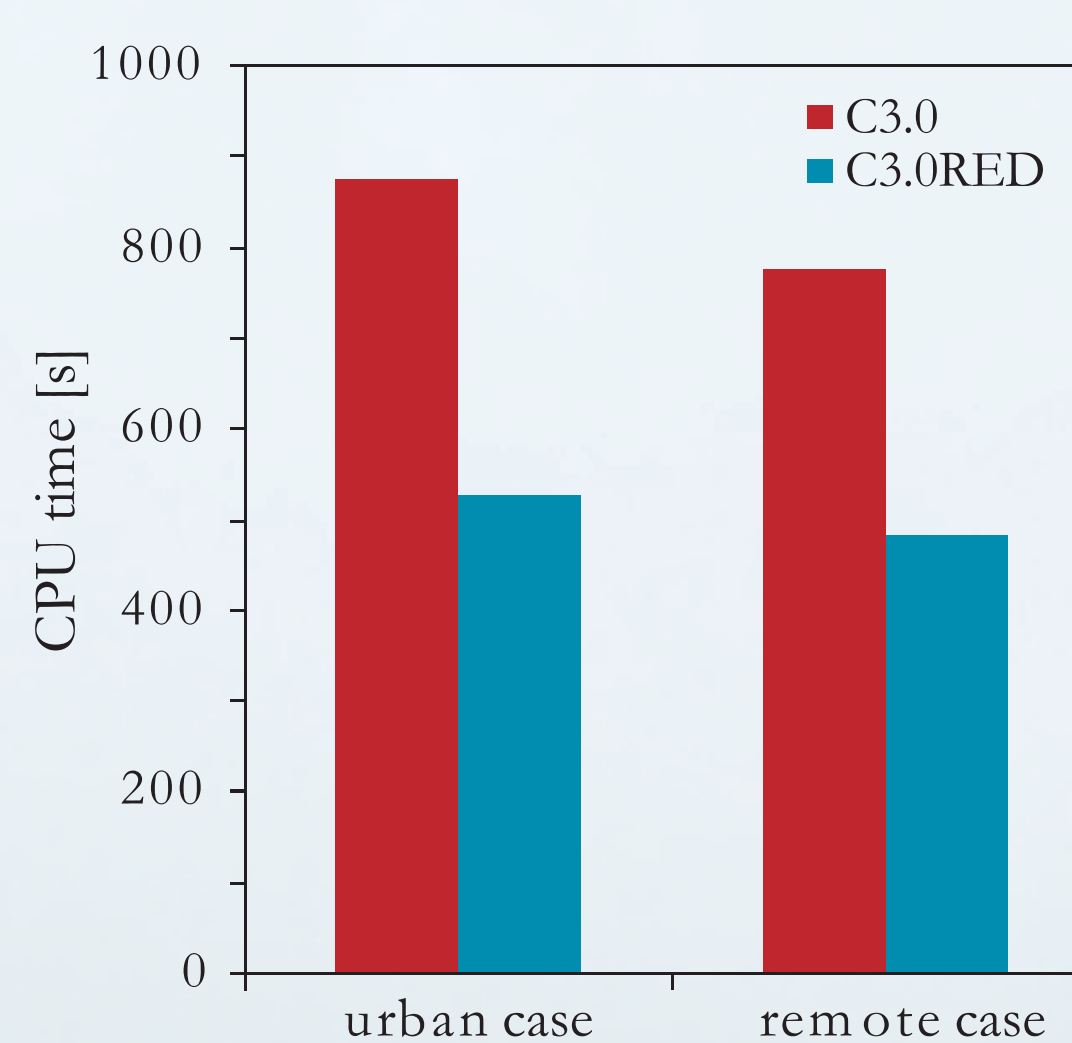


Figure 5: Comparison of the required CPU time of the full (red bars) and the reduced CAPRAM3.0i mechanism (blue bars) for the urban and remote model run.

Table 1: Mean percentage deviations [%] of some inorganic and organic target compounds between full and reduced RACM-MIM2ext/CAPRAM 3.0i mechanism (deviations calculated from the last 12 hours of the SPACCIM simulation).

Aqueous phase species	Remote	Urban
H <sub>2</sub> O	5.0	7.2
HO	5.2	10.7
H <sub>2</sub> O <sub>2</sub>	2.3	2.1
NO <sub>3</sub>	6.6	2.1
HNO <sub>3</sub> /NO <sub>3</sub>	3.9	0.1
H <sub>2</sub> SO <sub>4</sub> /SO <sub>4</sub> <sup>2-</sup>	0.02	3.0
H <sup>+</sup>	1.3	3.5
Formaldehyde CH <sub>2</sub> O	0.6	1.0
Ethylene glycol CH <sub>2</sub> (OH)CH <sub>2</sub> (OH)	1.4	3.0
Glyoxal CHOCHO/CH(OH)CH(OH)	1.6	0.8
Glycolaldehyde OHCCHO/CH(OH)CH <sub>2</sub> O	1.9	1.8
Methylglyoxal CH <sub>3</sub> COCHO/CH <sub>3</sub> COCH(OH) <sub>2</sub>	0.2	5.5
1,4-butanediol OHCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH	4.4	3.7
Acetic acid CH <sub>3</sub> COOH/CH <sub>3</sub> COO <sup>-</sup>	2.6	0.2
Glyoxylic acid CH(OH)COOH/CH(OH)COO <sup>-</sup>	5.1	10.0
Glycolic acid CH <sub>2</sub> (OH)COOH/CH <sub>2</sub> (OH)COO <sup>-</sup>	7.0	7.2
Pyruvic acid CH <sub>3</sub> COCOHOH/CH <sub>3</sub> COCO <sup>-</sup>	1.1	2.1
3-oxo-pyruvic acid CHOCOCOHOH/CHOCOCO <sup>-</sup>	6.2	4.9
Gas phase - mean deviation	1.8%	1.7%
Aqueous phase - mean deviation	2.8%	4.3%
Total (gaseous+aqueous phase) - mean deviation	2.5%	3.4%

## MUSCAT 2D-Application

In order to examine the applicability of the developed C3.0RED for later regional scale CTM applications, first test simulations were performed. For the model runs, the air pollution CTM MUSCAT (Multiscale Chemical Aerosol Transport Model, Wolke et al. [2004]) was further developed and applied in its 2D offline mode (one horizontal dimension has only one grid cell) using fixed meteorological conditions, i.e. the meteorology/cloud microphysics was prescribed time independent. The location of the cloud can be seen in Figure 8. The wind flow is from the left to the right boundary. The chemical species need about 30 minutes to stream through the cloud. The LWC is 0.5 g m<sup>-3</sup> in the center of the cloud and is reduced to the left, right and upper edge of the cloud on about one fifth. The droplet number is held constant on 300 cm<sup>-3</sup>. Model simulations were performed for two different chemical environments (urban/remote). Simulations with C3.0RED and a less complex inorganic aqueous phase chemistry mechanism (INORG, Sehili et al. [2005]), which focusses on sulfur chemistry only were performed. Simulation results were compared to briefly work out differences between typically operational used less explicit and more detailed chemistry mechanisms. For comparison of the chemical mechanisms, important chemical subsystems and parameters were investigated including e.g. major oxidants (OH, HO<sub>2</sub>, NO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>), S(VI), or the pH. Table 2 summarizes the differences between C3.0RED and a control run (no consideration of any cloud processes, equal to pure gas phase) in 2 reading points (M1: center of cloud, M2: 8 km behind cloud). The comparison has revealed that the INORG case is always less acidic (see Figure 7). This additional acidification using C3.0RED seems to be caused by the production of organic acids. Because of the differences in pH between C3.0RED and INORG, they result also in different regimes e.g. for the S(IV)-oxidation (see Figure 8).

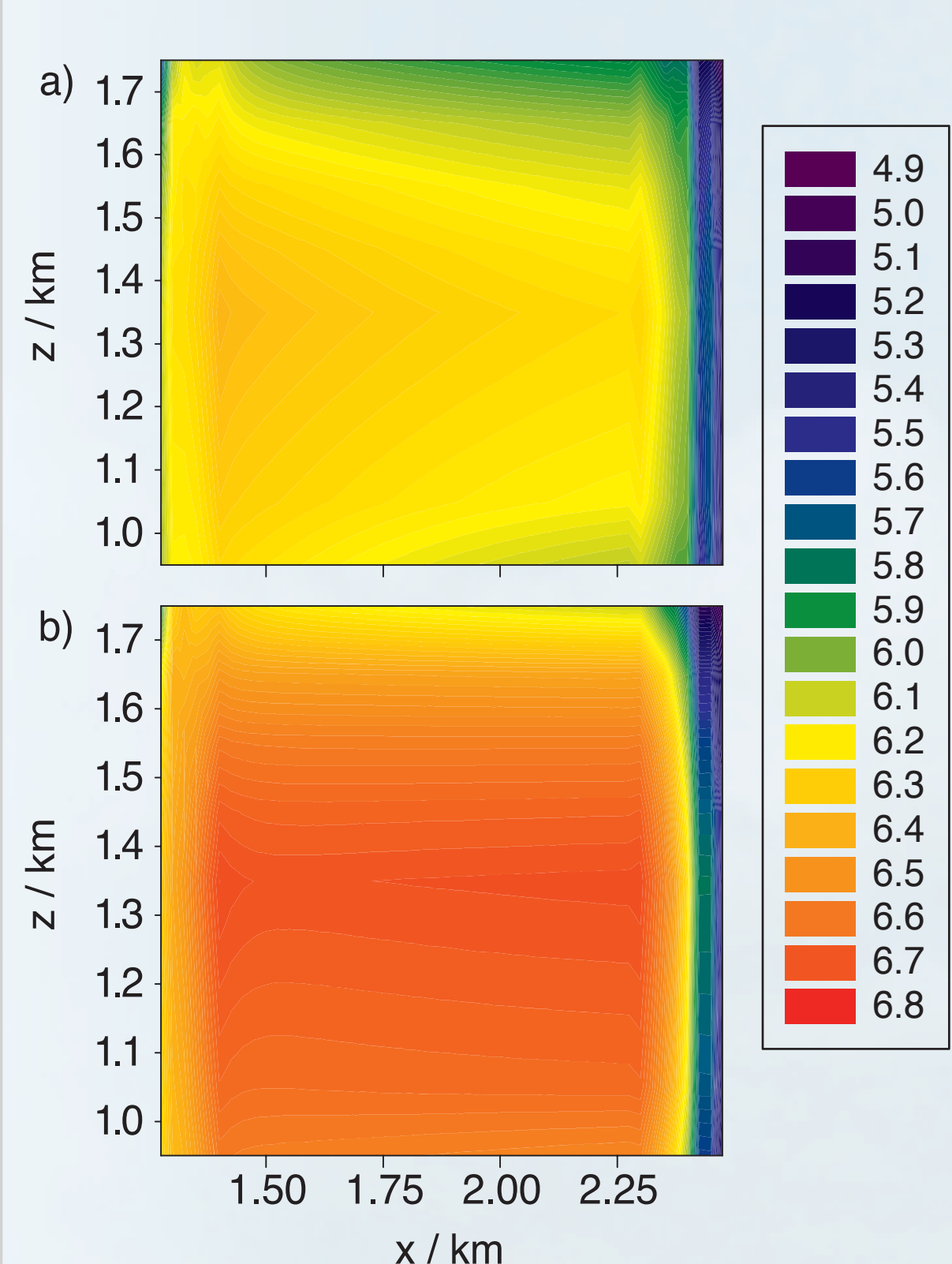


Figure 7: Distribution of pH within the cloud for a) C3.0RED and b) INORG at midnight for the remote case.

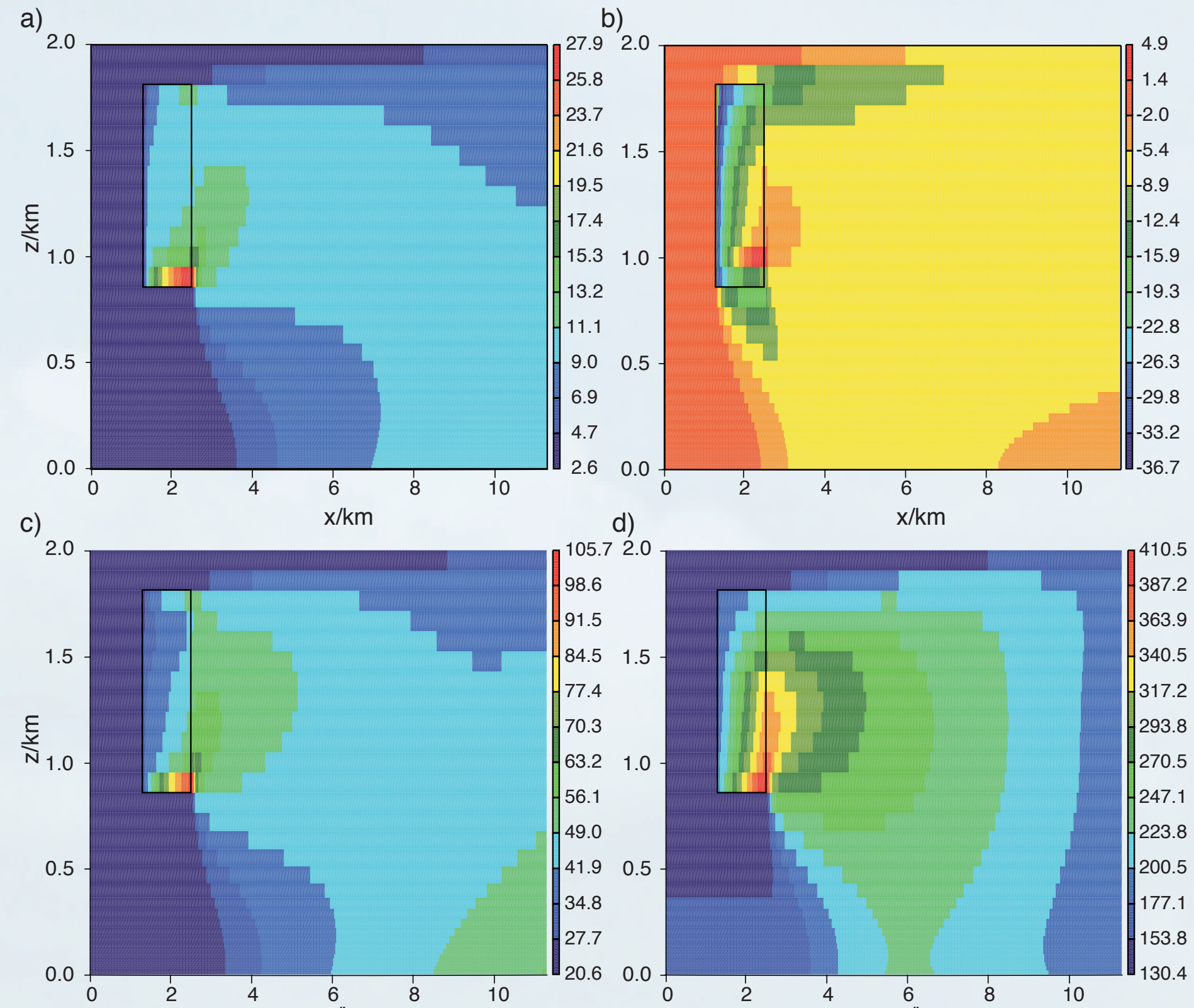


Figure 8: a) Modeled multiphase S(VI) mass [ $\mu\text{g m}^{-3}$ ] for the C3.0RED remote case at midnight. b) Difference of S(VI) mass in  $\mu\text{g m}^{-3}$  between INORG and C3.0RED (negative sign means more S(VI) mass for INORG). Modeled summed up mass of oxalate, glyoxylate, glycolate and pyruvate in  $\text{ng m}^{-3}$  at midnight for a) remote and b) urban environment. The cloud is located within the black

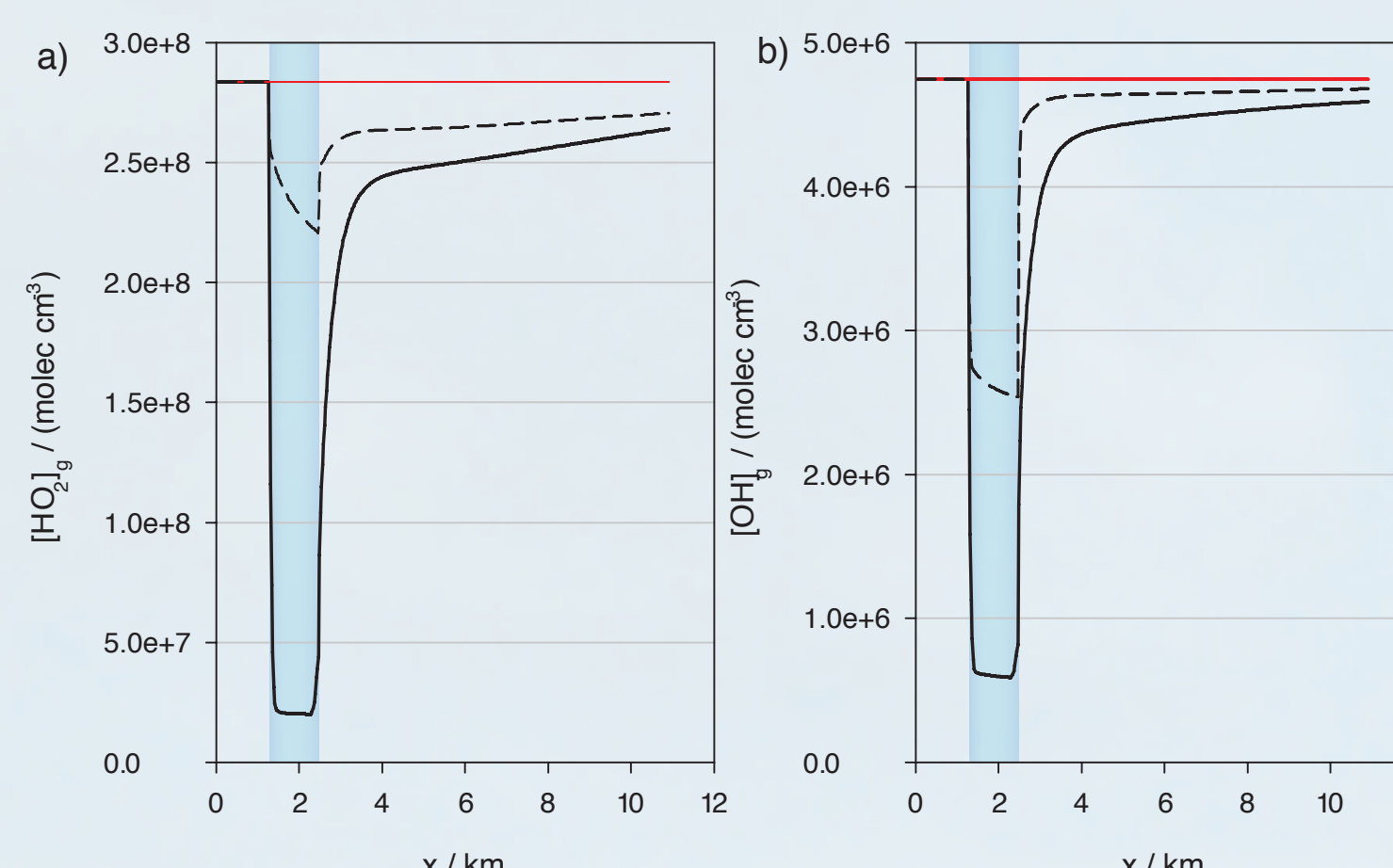


Figure 6: Gas phase concentration for HO<sub>2</sub> and OH for the urban scenario at highnoon. The cloud passage is marked with the blue rectangle.

Table 2: Relative difference between run without consideration of aqueous phase chemistry (RACM-MIM2ext only, no shading) and run with C3.0RED at 12 a.m. (at the 2 reading points: M1: center of cloud, M2: 8 km behind cloud). A negative sign represents a relative loss in C3.0RED.

Oxidant	M1, urban	M2, urban	M1, remote	M2, remote
OH	-87.4 %	-5.3 %	-61.8 %	-5.5 %
HO <sub>2</sub>	-92.9 %	-10.9 %	-97.4 %	-4.5 %
H <sub>2</sub> O <sub>2</sub>	-99.6 %	-75.8 %	-82.4 %	-17.9 %
O <sub>3</sub>	-2.0 %	-3.9 %	-3.1 %	-2.5 %
NO <sub>3</sub> (24:00)	-97.4 %	-27.3 %	-16.7 %	14.9 %

## Summary and Outlook

A manual and automatic chemical mechanism reduction was performed in order to develop a reduced CAPRAM 3.0i mechanism. For the mechanism reduction manual and automatic techniques were applied in order to provide a less computationally intensive mechanism which is operational in regional scale CTMs and accurately represents the main characteristics of inorganic and organic aqueous phase processes occurring in tropospheric warm clouds. The developed reduced mechanism with less than 200 reactions is nearly a factor of 4 smaller than the full CAPRAM 3.0i. Most of the chemical reduction potential has been realised in the organic chemistry with 398 minor important reactions. Moreover, the number of aqueous phase species decreased from 380 in the full CAPRAM 3.0i mechanism to 130 in the final reduced version. The calculated percentage deviations between the two mechanisms are mostly below 5% for the most target compounds. Comparisons of the required CPU times between the full and final reduced mechanism showed reductions of approximately 40%. In order to examine the applicability of the developed reduced mechanism for later regional scale applications, 2D test simulations with the MUSCAT CTM were performed using fixed meteorological conditions. Simulations with the reduced CAPRAM 3.0i mechanism and a less complex inorganic aqueous phase chemistry mechanism (INORG) were compared to evaluate the effects of more detailed chemistry. The model results show considerable differences in the multiphase oxidation budget and the inorganic mass processing. Prospectively, the reduced mechanism represents the basis for studying aerosol cloud processing effects on regional scale and will allow also more adequate interpretation of field data. Prospectively, the final reduced aqueous phase mechanism represents the basis for studying cloud effects on regional scale with CTMs such as the COSMO-MUSCAT. Finally, the application of this new mechanism in various model studies will be essential for a better understanding of multiphase aerosol cloud processing effects on regional scale in future CTM applications and will allow also more adequate interpretation of field data.

## References

Ervens, B. et al. (2003) Journal of Geophysical Research, 108, Mauersberger, G. (2005) Atmospheric Environment, 39, 4341-4350  
 Sehili, A.M. et al. (2005) Atmospheric Environment, 39, 4403-4417  
 Tilgner, A. and Herrmann, H. (2009) submitted to Atmospheric Environment.  
 Wolke, R. et al. (2004), in Parallel computing: Software technology, algorithms, architectures and applications, G. R. Joubert, W. E. Nagel, F. J. Peters, and W. V. Walter, Eds., Elsevier, 363-370.  
 Wolke, R. et al. (2005) Atmospheric Environment, 39, 4375-4388