Modelling the multiphase chemical processing of Monoethanolamine from industrial CCS processes in tropospheric aqueous particles and clouds

Andreas Tilgner, Roland Schrödner, Peter Bräuer, Ralf Wolke, and Hartmut Herrmann

Leibniz-Institute for Tropospheric Research (TROPOS), Permoserstr. 15, D-04318 Leipzig, Germany

✉ tilgner@tropos.de

Introduction and Motivation

Using amine based solvent technology is an option to realise CO_2 capture from the exhaust of power plants. Amines such as Monoethanolamine (MEA) may potentially be released in trace amounts during the carbon capture and storage (CCS) process. In order to investigate the tropospheric chemical fate of MEA released from CO_2 capturing processes and its potentially harmful oxidation products such as formed nitrosamines and nitramines, multiphase modelling was performed. Furthermore, a reduced mechanism for future 3D dispersion model applications was developed in the present study. Based on former laboratory investigations and mechanism developments [1], an up-to-date multiphase mechanism describing the gas and aqueous phase chemistry of MEA was developed. Finally, the complex mutliphase mechanism was applied in the parcel model SPACCIM (Spectral Aerosol Clouds Chemistry Interaction Model, [2]) and the reduced mechanism was applied in first 2D-simulations using the COSMO-MUSCAT model [3]. The modelling work was specifically designed to resemble characteristic meteorological conditions present at a planned power plant with CO_2 capture in the area close to Bergen, Norway (see Fig.1).

Fig. 1: Industrial site at Mongstad (Norway).

Mechanism and Modelling

The developed multiphase phase mechanism of MEA and its oxidation products was coupled to the existing multiphase chemistry mechanism RACM-MIM2ext-CAPRAM3.0i-red [4] and the CAPRAM Halogen Module 2.0 [5]. Overall, the multiphase mechanism comprises 1276 chemical processes including 668 gas and 518 aqueous phase reactions as well as 90 phase transfers. The multiphase amine module contains in total 138 processes. The final mechanism was applied in the parcel model SPACCIM. Simulations were performed for summer (S) and winter (W) conditions (simulating high and low photochemical activity), different environmental trajectories (MM/MR: marine air mass + marine/remote avdvection). Additionally, simulations were performed (i) with the full MEA mechanism (MEAgas+aq) (ii) with the gas phase part of the MEA mechanism only (MEAgas) and, (iii) only with the RACM-MIM2ext mechanism coupled to the gas phase part of the MEA mechanism (RACM+MEAgas). The two latter mechanisms were used in order to characterise the importance of the aqueous phase processes and the partitioning into the aqueous phase in comparison to pure gas phase mechanisms usually applied in regional scale dispersion models. In all scenarios, an air parcel moves along a predefined trajectory passing 4 cloud events (2 times at noon and 2 times at midnight) for about 2 hours each so that the air mass is subjected to a typical tropospheric in-cloud residence time of about 15%. Intermediate non-cloud peroids are considered at 80% RH representing typical conditions in the Mongstad area. Moreover, sensitivity studies were performed studying the impact of apllied mass accommodation coefficient values (α) for multiphase partitioning and processing of MEA and its products.
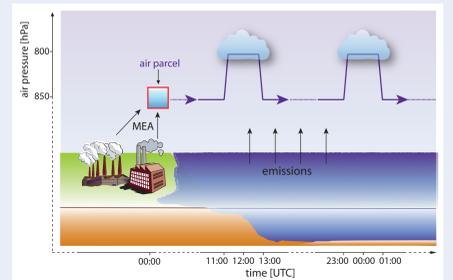

Fig. 1: Scheme of the modeled MMS/MMW scenario.

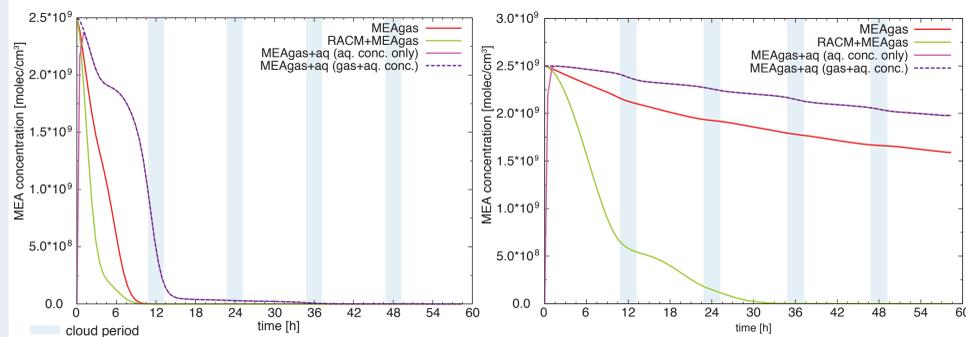## Results and Discussion

■ Multiphase oxidation of MEA

Fig. 2: Modelled monoethanolamine (MEA) concentration profiles (in molecules cm^{-3}) for the scenarios MMS (summer case, left) and MMW (winter case, right) in the different mechanism cases.
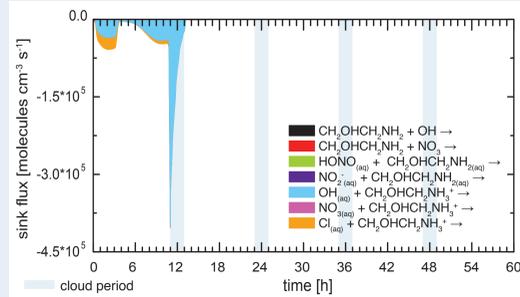

Fig. 3: Modelled time-resolved sink fluxes for MEA during the simulation period of 60 hours of the MMS scenario (MEAgas+aq).

Model studies showed (see Fig.2 and Fig.3):
➢Substantial MEA oxidation under daytime summer cloud conditions (MMS)
➢Degradation fluxes significantly lower in the winter case with just 20% of the initial MEA concentration oxidised after 60h (MMW)
➢An increased tropospheric lifetime due to the less effective aqueous phase degradations under consideration of aq. phase processes implicating that deposition will be a relevant removal pathway during winter
➢Aq. OH most important oxidant for MEA [82% contribution to the MEA oxidation (MMS)];
➢Gas and aq. NO_3 radical turnovers not important for the fate of MEA [<1% in all cases]
➢Aq. Cl radical reactions important sink under winter conditions particularly in the aqueous particles [39% contribution to the MEA oxidation (MMW)]
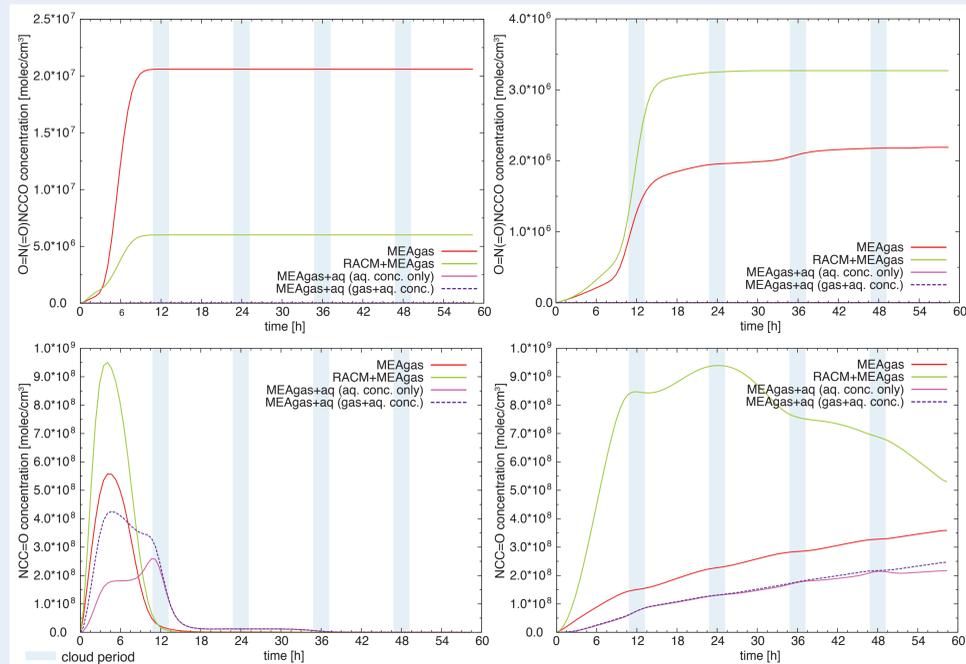
■ MEA oxidation products

Fig. 4: Modelled nitramine (O=N(=O)NCCO, top) and nitramide (NCC=O, down) concentration profiles (in molecules cm^{-3}) for the model scenarios MMS (left) and MMW (right) in the different mechanism cases.

Model studies showed (see Fig.4 and Fig.6):
➢Gas and aqueous formation of N-nitroso-MEA not important for the primary amine MEA
➢MEA-Nitramine (O=N(=O)NCCO) formed exclusively in the gas phase on a relatively short timescale
➢Formation of harmful species suppressed due to treament of aq. chemistry / predicted concencentrations (few 10^4 molec. cm^{-3}) with consideration of aq. phase processes far below the limit of longterm exposure ($2 \cdot 10^5$ molec. cm^{-3})
➢Corresponding aldehyde (NCC=O) is effectively formed and oxidised, particularly under daytime cloud conditions
➢Produced imines are rapidly degraded in tropospheric clouds leading to the formation of smaller amines
➢Sensitivity studies with differnt α-values revealed a significant impact on the predicted conc. levels of MEA and particularly the harmful MEA-nitramine (conc. variation beween 10^4 and few 10^6 molecules cm^{-3} for O=N(=O)NCCO)
→ Experimentally obtained α's of soluble amines such as MEA are a must to improve the current model results

■ Reduced MEA chemistry mechanism

Tab. 1: Number of processes and chemical species after each reduction step (RS) compared to the full mechanism (RS0).

Reduction step	0	1	2	3	4
Species	544	541	501	310	215
Gas	270	267	267	133	123
Aqua	274	274	234	177	92
Reactions	1276	1273	1224	666	447
Gas phase	668	665	664	315	303
Phase Transfer	90	90	89	57	32
Aqueous phase	396	396	350	219	74
Dissociations	122	122	121	75	38

Remarks: RS1: Reduction of MEA gas phase chemistry
RS2: Reduction of MEA aq. phase chemistry
RS3: Reduction of the Halogen Module 2.0
RS4: Further reduction of the C3.0i-red/HM2.0
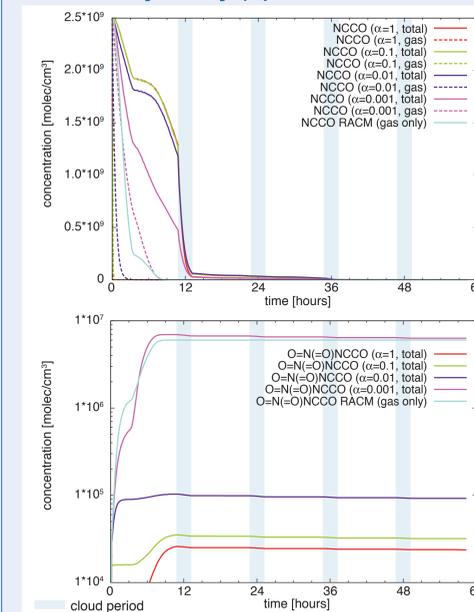
■ Sensitivity study (α)

Fig. 6: Sensitivity study with different α-values (MMS), modelled concentration of MEA (top) and MEA-Nitramine (down).
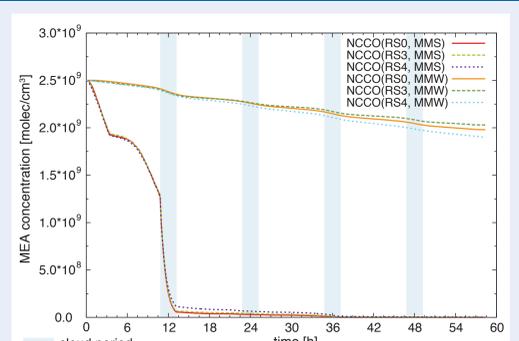

Fig. 5: Modelled total (gas + aq. phase) concentration of MEA (NCCO), using the full mechanism (reduction step 0 (RS0)) and 2 condensed mechanisms (RS3/RS4) under MMS/MMW conditions.

Performed comparison of the full and reduced mechanism showed:
➢Deviations between the full and condensed mechanisms relatively small for MEA and its main oxidation products
➢Reduction of the total required CPU time by approx. 45 %
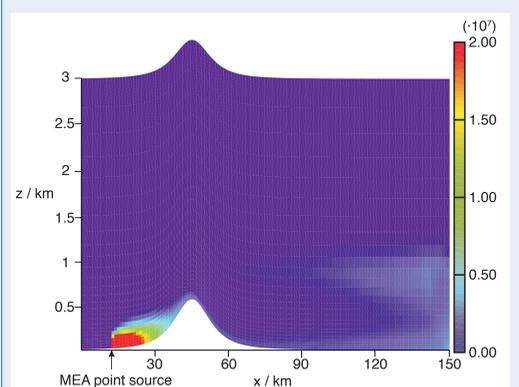
■ First 2-D COSMO-MUSCAT study

Fig. 7: Vertical cross section of the concentration of MEA (gas + aq. phase) in molecules cm^{-3} at 12:00 (after 36 hours of simulation time). Calculations were conducted with the fully coupled multiphase transport model COSMO-MUSCAT. The main wind direction is from left to right. An orographic cloud is evolving at the top of the hill.

Summary

Model simulations revealed the importance of both clouds and aqueous particles for the multiphase chemical processing of MEA and its products. Due to the shifted partitioning of MEA towards the aqueous phase, the model investigations implicate that aqueous oxidation by OH radicals represents the main sink for MEA under daytime cloud summer conditions. Reaction flux analyses have shown that under aqueous particle conditions, the Cl radical represents also an important oxidant. Moreover, the simulations showed that the aqueous formation of N-nitroso-MEA is an irrelevant process under tropospheric conditions. MEA oxidations are quite restricted under low photochemical winter conditions leading to much longer tropospheric residence times. Additionally, the model simulations implicated that the aqueous phase reduces substantially the formation of harmful compounds such as MEA-nitramine in the gas phase. Thus, simulations without aqueous phase chemistry treatment were characterised by much higher concentrations of MEA-nitramine implicating that pure gas phase simulations provide elevated "worst case concentrations" and might be used for "upper limit" estimations of harmful MEA products. Furthermore, performed sensitivity studies on the importance of the applied mass accommodation coefficients (α) have revealed that the applied α-value in the performed multiphase chemistry simulations is a very crucial parameter, e.g., for MEA and particularly for the MEA-nitramine, which can significantly influence the predicted concentration levels. To provide a condensed mechanism applicable for regional scale dispersion modelling, a manual mechanism reduction was performed. The developed reduced mechanism contains just 303 gas and 112 aqueous phase reactions and describes adequately the chemical fate of MEA and its key oxidation products. The required CPU costs are reduced by about 45% compared to the full mechanism. Finally, first 2D-simulations were performed using the COSMO-MUSCAT CTM investigating the chemical fate and dispersion of MEA and its partly harmful oxidation products.

References

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[2] Wolke, R. et al. (2005) Atmos. Environ. 39 (23-24), 4375-4388.
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