Modelling the Multiphase Formation of High H_2O_2 Concentrations Observed during Winter Haze Periods in the NCP

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Introduction

During winter, the North China Plain (NCP) is frequently characterised by severe haze conditions connected with extremely high $PM_{2.5}$ and NO_x concentrations, i.e. strong air pollution. Tropospheric haze particles are a complex multiphase and multicomponent environment, in which multiphase chemical processes are able to alter the chemical aerosol composition and deduced physical aerosol properties, and can strongly contribute to air pollution. Hence, as with around 400 million inhabitants, the NCP is one of the most populated areas woldwide tropospheric haze particle related chemistry events have a high influence on human health. Despite many past investigations, the chemical haze processing is still uncertain and represents a challenge in atmospheric chemistry research. Recent NCP studies during haze periods in autumn/winter 2016 and 2017 [1] have measured unexpected high H_2O_2 concentrations of about 1 ppb suggesting H_2O_2 as a potential contributor to secondary $PM_{2.5}$ mass, e.g., due to sulphur(IV) oxidation in haze particles. However, the classical gas-phase H_2O_2 formation under such NO_x concentrations is inhibited suggesting multiphase chemistry as key to H_2O_2 production. Hence, the present study aims at the examination of potential multiphase H_2O_2 formation pathways, and feedback on sulphur(IV) oxidation.

Multiphase modelling and mechanism development

- Multiphase chemistry simulations of the measurement campaign with the box model SPACCIM [2]
- Usage of the multiphase chemistry mechansim MCM/CAPRAM together with advanced modules [3-6]
- Simulations of three appropiate periods characterised by high H_2O_2 concentrations
- Initial simulations demonstrated that in-particle TMI chemistry plays key role in H_2O_2 production (> 60%)
- H_2O_2 concentrations of initial simulations are more than one magnitude lower than those measured
- Studies showed that interconnection of TMIs with humic like substances can be a source for H_2O_2 [7]
- Multiphase chemistry mechanism is extended based on available literature data
- Consideration of advanced HO_x chemistry in haze particles.enabling higher in-situ H_2O_2 formations

Table1. Perfomed model simulations.

Model run	Description
without improvement	MCMv3.2-CAPRAM4.0α/HM2.1/AM1.0
base case	MCMv3.2-CAPRAM4.0α/HM2.1/AM1.0 with added iron-HULIS chemistry
low soluble TMI	base case with low TMI soluble fraction
high soluble TMI	base case with high TMI soluble fraction
without TMI chemistry	run without TMI chemistry

Key iron-HULIS complex reactions

$HULIS + H_2O \rightleftharpoons HULIS^- + H^+ + H_2O$ (R-I)
$Fe^{2+} + HULIS^- \rightleftharpoons FeHULIS^+$ (R-II)
$FeHULIS^+ + O_2 \rightarrow FeHULIS^{2+} + O_2^-$ (R-III)
$FeHULIS^+ + O_2^- \rightarrow FeHULIS^{2+} + H_2O_2$ (R-IV)
$FeHULIS^+ + H_2O_2 \rightarrow FeHULIS^{2+} + OH + OH^-$ (R-V)
$FeHULIS^{2+} + h\nu + O_2 \rightarrow Fe^{2+} + HULIS + HO_2$ (R-VI)

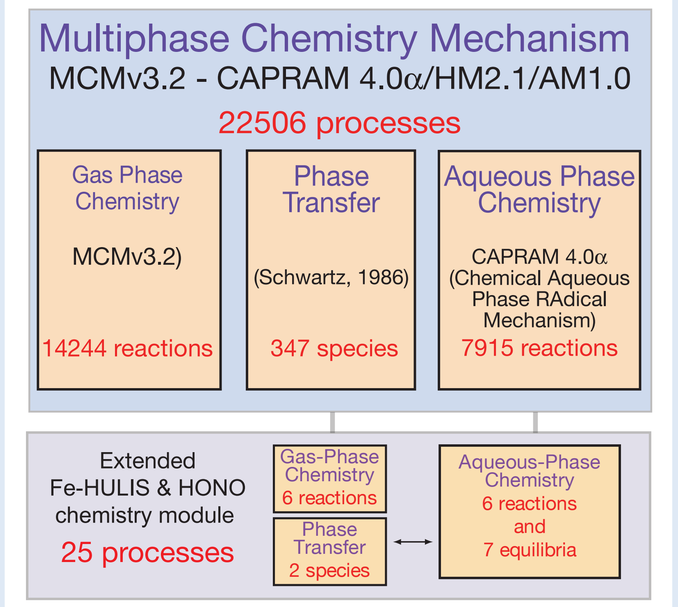

Fig. 1: Scheme of the applied multiphase chemistry mechanism and the newly developed reaction module.

Results & Discussion

H_2O_2 field observations

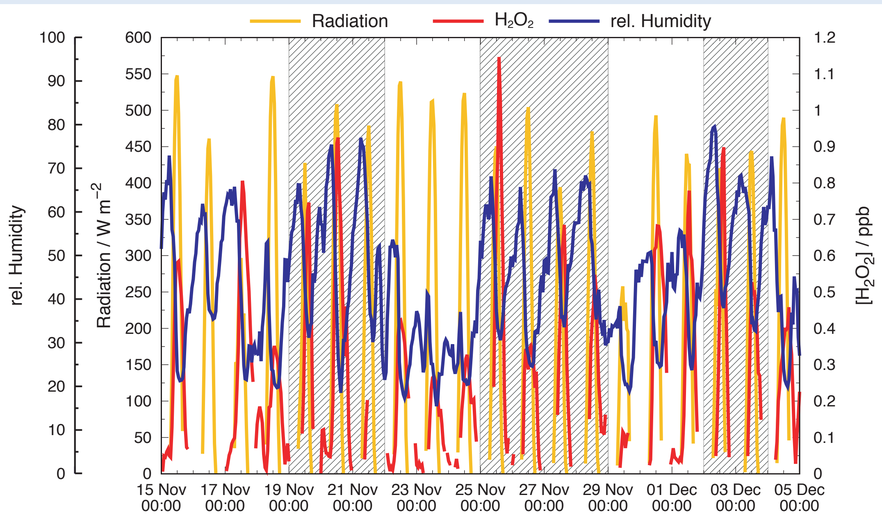

Fig. 2: Measured global radiation, relative humidity and H_2O_2 concentration during the selected modelling periods (gray shaded areas).

- Observed dependencies of daytime H_2O_2 production rates on sunlight intensity and relative humidity
- Indication of aqueous photochemical H_2O_2 formation

Modelled sulfate formation with MCM/CAPRAM

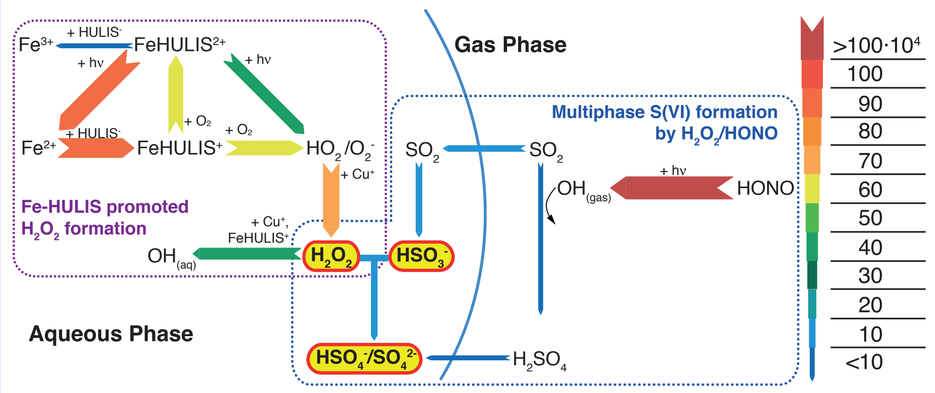

Fig.4: Average multiphase source and sink fluxes (in molecules cm^{-3} s^{-1}) of H_2O_2 and sulfate formation derived from the second model period (25th-29th Nov). The width and color of arrows indicate the magnitude of the mass flux. The reactant is given above or below the arrows.

- Modelled H_2O_2 concentrations match with the field data
- Confirmation of efficient H_2O_2 formation via the new Fe-HULIS complex chemistry
- Model results demonstrate that sulfate formations during haze events in the NCP are a complex multiphase reaction sequence (Fig. 4)
- Increased S(IV) concentration in the early morning when H_2O_2 increases and photolysis of HONO is active

H_2O_2 process modelling with MCM/CAPRAM

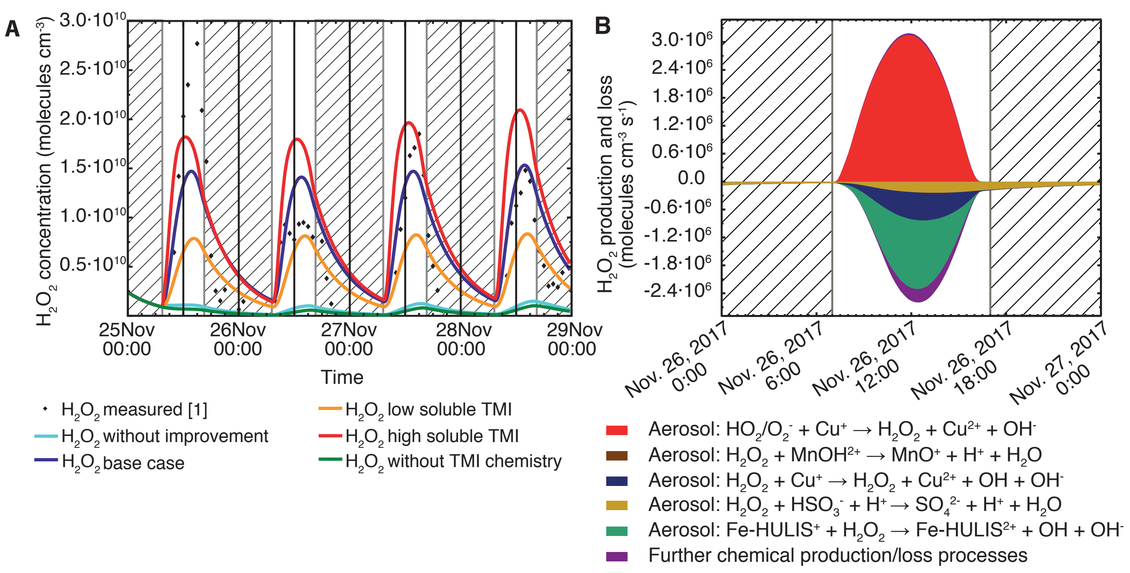

Fig. 3: The measured and simulated gas-phase H_2O_2 concentrations (A) during the second model period (25th-29th Nov) and modelled multiphase chemical sink and source fluxes of H_2O_2.(B) (base case) during the second model day.

Summary and Outlook

- New module developed containing advanced TMI-HULIS chemistry promoted HO_x formation and coupled to the MCMv3.2-CAPRAM4.0a mechanism
- Box model sudies with SPACCIM focusing on multiphase formation of H_2O_2 and its feedback on sulfur(VI) formation under the measured haze conditions
- Very good agreements of the modelled H_2O_2 concentrations with field data
- Modelled H_2O_2 formation depends strongly on soluble TMI content
- Chemical flux analyses reveals that most H_2O_2 is produced in-situ within the haze particles
- Demonstration that photochemistry between HULIS and TMIs in haze particles is an important H_2O_2 source leading to increased particle sulfate formation

References

[1] **Ye** et al., (2018)., Environ. Sci. Technol. Lett., 5, 757-763; [2] **Wolke** et al., (2005) Atmos. Environ. 39, 4375-4388; [3] MCM webpage (http://mcm.leeds.ac.uk/MCMv3.2/); [4] **Bräuer** et al. (2019) Atmos. Chem. Phys., 19, 9209-9239; [5] **Hoffmann** et al. (2018) Phys. Chem. Chem. Phys. 20, 10960-10977; [6] **Hoffmann** et al. (2019) Environ. Sci. Technol., 53, 771-778; [7] **Gonzalez** et al. (2017) Environ. Sci. Technol. 51, 7676-7685.