

# Bulk aqueous phase kinetic and chamber studies leading to new CAPRAM modules and applications

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In this presentation, recent experimental work on aqueous chemistry centered around organics in atmospheric particles is described which was performed to lead to new modules and improvements for the atmospheric aqueous mechanism CAPRAM. *Isoprene*: Gas phase oxidation of isoprene under low NO<sub>x</sub> conditions leads to the formation of oxygenated organic hydroperoxides, ISOPOOHs and ISOPOOH<sub>2</sub> that can chemically interact with aerosol particles and clouds. Recent investigations at TROPOS are aimed at the multiphase chemistry of these compounds, particularly, on their potential to act as source of aqueous OH and aqSOA. For this goal, the two most abundant isomers of isoprene-derived hydroxy hydroperoxides (ISOPOOH) were synthesized to investigate both aqueous-phase kinetic as well as multiphase partitioning using chamber studies. A suitable OH scavenger, analysed by gas chromatography mass spectrometry (GC-MS), was used to determine the OH radical production rate of the thermic decay, the photolysis and a Fenton type reaction of ISOPOOH with iron(II) salts in aqueous solution were determined and compared. A series of aerosol chamber experiments was performed to investigate the gas-particle partitioning of the synthetic standards as well as their oxidation products for various inorganic seed particles under different conditions. Connected CAPRAM work shows that multiphase ISOPOOH/ISOPOOH<sub>2</sub> chemistry can act as an important source for aqueous OH and aqSOA in both aerosols and clouds.

*Biomass burning (BB)* is a significant air pollution source, with global, regional and local impacts on air quality, public health and climate. Anhydrosugars and methoxyphenols are the most important BB products emitted into the atmosphere. A CAPRAM BB-module treating the oxidation of such compounds has been developed based on the kinetics data from the laser flash photolysis measurements in our lab. The developed CAPRAM-BB module, as the first of its kind, is applied for different BB simulation cases investigating both the tropospheric processing of BB compounds and their contribution to other aqSOA compounds.

*H<sub>2</sub>O<sub>2</sub>*: During winter, the North China Plain (NCP) is frequently characterized by severe haze conditions. Recent NCP studies during autumn/winter 2017 haze periods have revealed unexpected high H<sub>2</sub>O<sub>2</sub> concentrations of about 1 ppb suggesting H<sub>2</sub>O<sub>2</sub> as a potential contributor to secondary PM<sub>2.5</sub> mass, e.g., due to sulfur(IV) oxidation<sup>1</sup>. However, the multiphase H<sub>2</sub>O<sub>2</sub> formation under such NO<sub>x</sub> concentrations is still unclear. Therefore, the present study aimed at the examination of potential multiphase H<sub>2</sub>O<sub>2</sub> formation pathways, and the feedback on sulfur

oxidation by combined field, chamber and model studies. A series of chamber experiments with particles containing Suwanee River Fulvic Acid (SRFA) as a proxy for humic-like substances (HULIS) under high NO<sub>x</sub> and high SO<sub>2</sub> conditions were performed. Monitored gas-phase H<sub>2</sub>O<sub>2</sub> concentrations increased during UV-radiation compared to blank experiments without SRFA, indicating a photochemical mechanism involving HULIS. The role of transition metal ions was shown by significantly lower gas phase H<sub>2</sub>O<sub>2</sub> concentrations with a suitable chelating agent present in the seed solution. Performed simulations with an new advanced HONO and HO<sub>x</sub> CAPRAM mechanism scheme are able predict high in-situ H<sub>2</sub>O<sub>2</sub> formations in haze particles and show a good agreement with field data. Rate analyses reveal that a huge fraction of the multiphase HO<sub>2</sub> radicals, formed via an efficient TMI-HULIS chemistry, and nearly all of the subsequently formed reaction product H<sub>2</sub>O<sub>2</sub> is produced in-situ within the haze particles and does not origin from the gas phase. Finally, the model studies show that, during the morning hours, the aqueous-phase reaction of H<sub>2</sub>O<sub>2</sub> with S(IV) contributes considerably to S(VI) formation beside the HONO related formation of sulfuric acid by OH in the gas-phase.

## References

- 1 Ye, C. *et al.* High H<sub>2</sub>O<sub>2</sub> concentrations observed during haze periods during the winter in Beijing: Importance of H<sub>2</sub>O<sub>2</sub> oxidation in sulfate formation. *Environ. Sci. Technol. Lett.* **5**, 757-763, doi:10.1021/acs.estlett.8b00579 (2018).