Modeling the photochemical formation of high H_2O_2 concentrations and secondary sulfate observed during winter haze periods in the NCP

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- North China Plain (NCP) frequently characterized by severe haze conditions connected with extremely high $PM_{2.5}$ and NO_x concentrations during winter
- NCP one of the most populated regions worldwide where polluted haze periods cause direct health effects
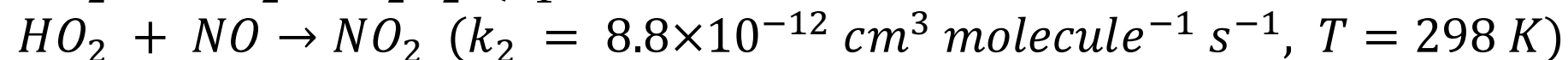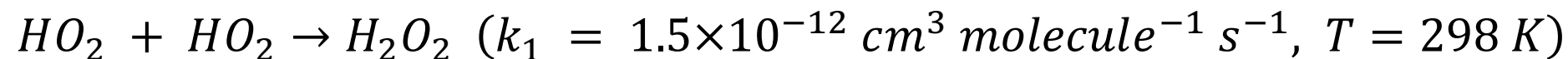

Wangdu viliiage (Dec. 2017)

SRE-CAS measurement site near Wangdu (Dec. 2017)
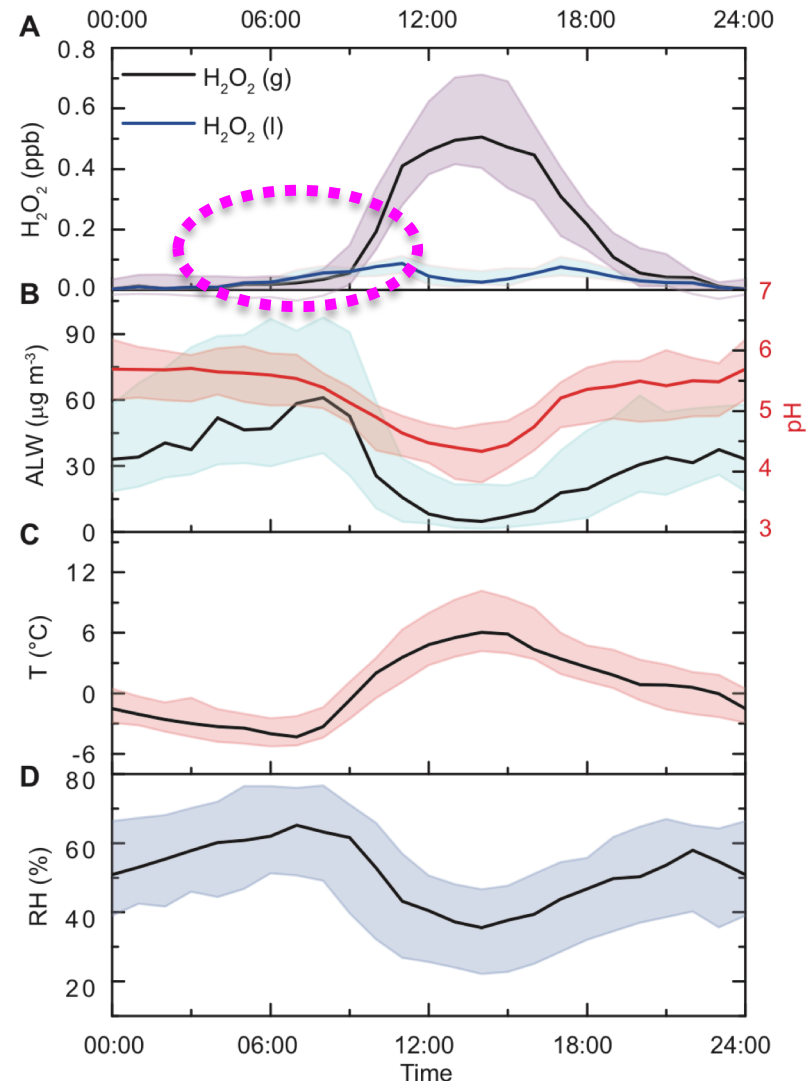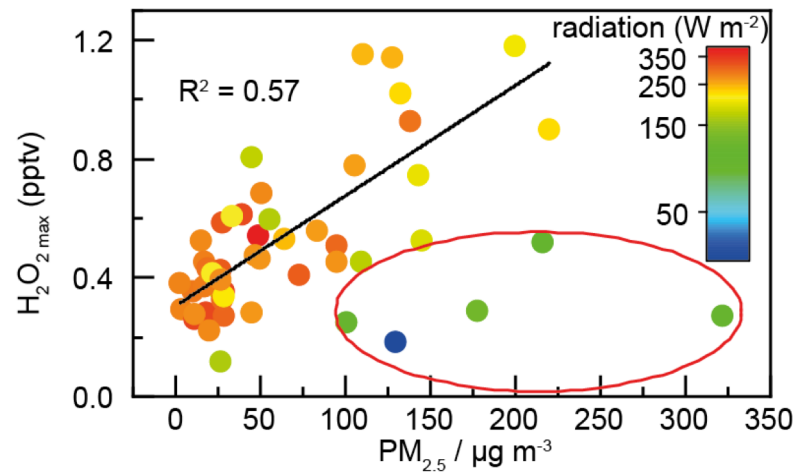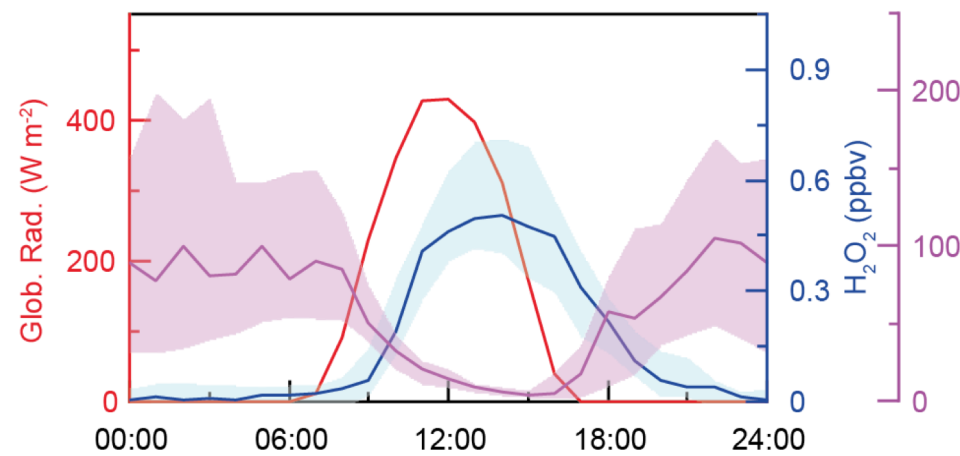
Source: Can Ye (2017)

Motivation (2)

- Despite many investigations, chemical haze processing still uncertain
- Particularly, the oxidants budgets and the strong formation of secondary inorganic aerosol (SIA) components is still under debate

- Recent NCP field observations during autumn/winter 2016 and 2017 haze periods showed unexpected high H_2O_2 concentrations of ~1 ppb (*Ye et al., 2018*)
- *Ye et al. (2018)* suggested H_2O_2 as potential contributor to secondary $S(VI)/PM_{2.5}$
- Multiphase H_2O_2 formation for such NO_x (daytime NO > 1 ppb) conditions unknown
- Gas-phase formation via typical HO_2 recombination impossible under high NO_x

$$HO_2 + HO_2 \rightarrow H_2O_2 \ (k_1 = 1.5 \times 10^{-12} \ cm^3 \ molecule^{-1} \ s^{-1}, \ T = 298 \ K)$$
$$HO_2 + NO \rightarrow NO_2 \ (k_2 = 8.8 \times 10^{-12} \ cm^3 \ molecule^{-1} \ s^{-1}, \ T = 298 \ K)$$

Goal: Examination of potential **multiphase H_2O_2 formation** pathways under haze conditions and its **feedbacks on S(IV) and $PM_{2.5}$**

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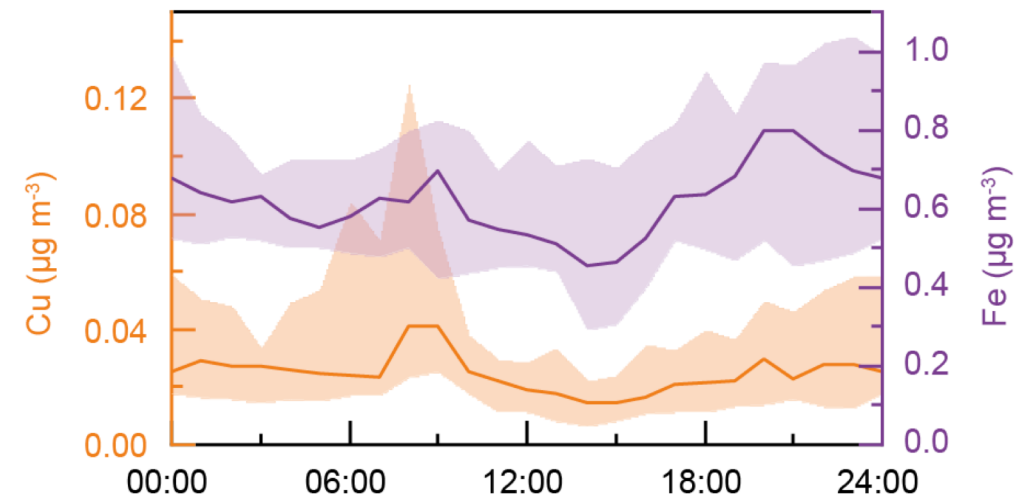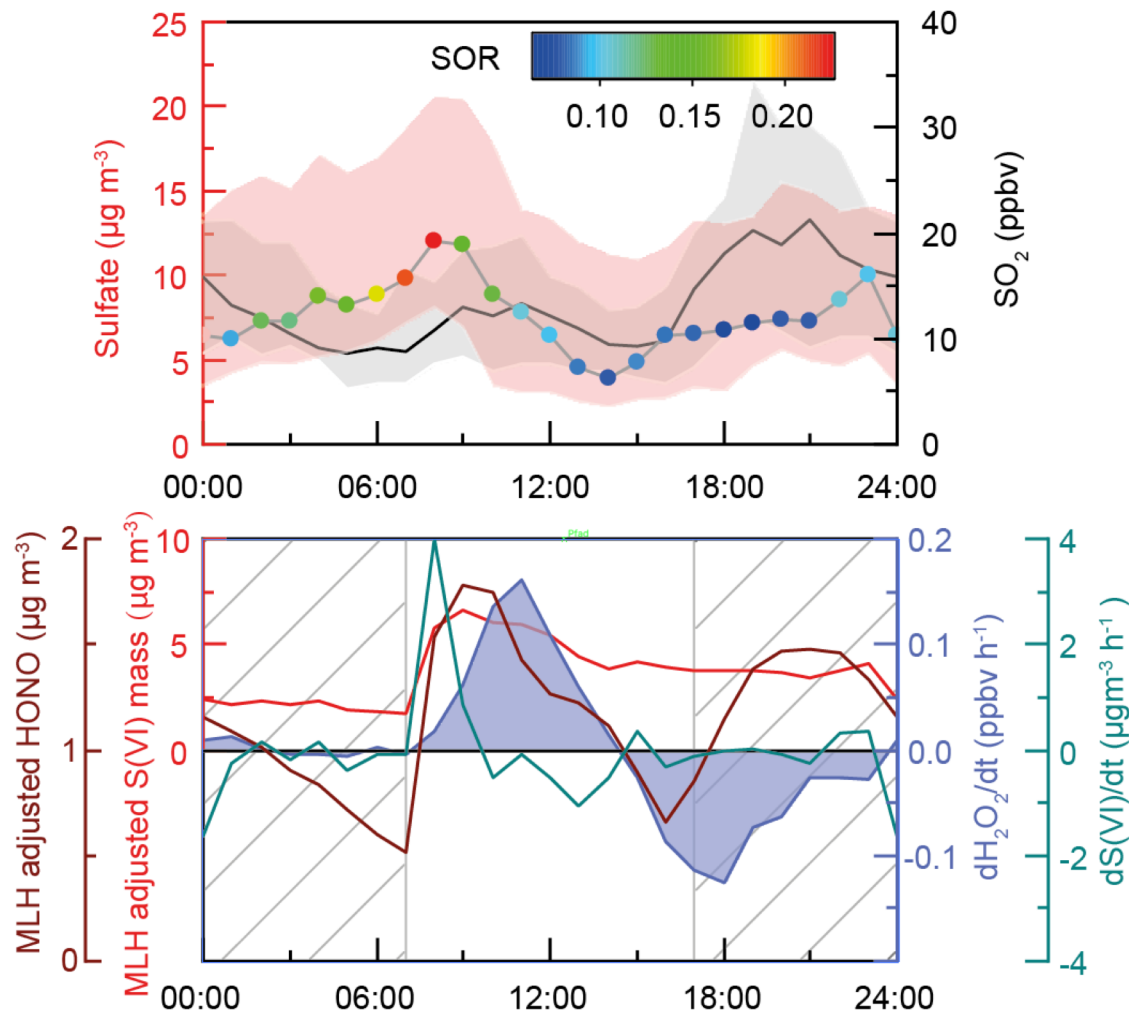
- High daytime [H_2O_2] up to 1 ppb

- Observed dependencies of the daytime H_2O_2 production rates on both solar radiation and RH/ALWC

- High aqueous aerosol particle [H_2O_2] in the morning under low T & high RH/ALWC

→ **Indication an aqueous photochemical H_2O_2 formation**
(incl. redistribution of H_2O_2 between particle-phase and gas phase

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- Increased S(IV) concentration in the early morning when $H_2O_{2(aq)}$ began to increase and HONO photolysis is active

- Increased morning SOR levels coincide with increased TMI's levels and increasing radiation

→ **TMI-related photochemistry**

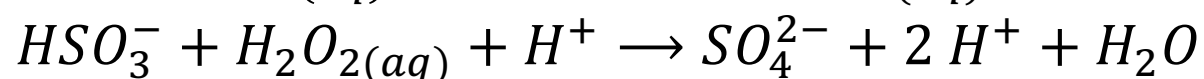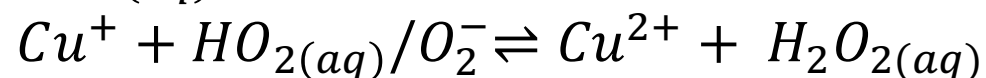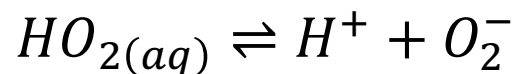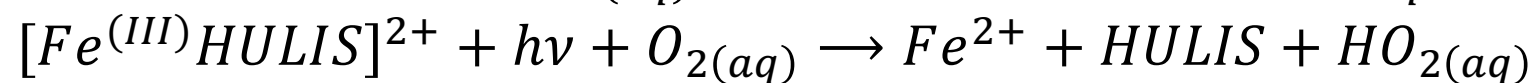**TROPOS**

Multiphase modelling of the campaign data

- First model studies failed to model the high H_2O_2 concentrations observed in the fields **Chemical mechanism developments needed!**

- Known from literature:
  1. H_2O_2 effectively formed in natural surface waters exposed to sunlight (photochemistry of organic material, chromophores as humic substances, and TMIs suggested to be responsible for photochemical H_2O_2 formation; *Cooper and Zika (1983), Lueder et al. (2020)*)
  2. Photochemical cycling of Fe(II)-Fe(III) complexes leading to H_2O_2 formation in atmospheric cloud/fog water (e.g., *Zuo and Hoigné (1993), Faust et al. (1993)*)

- Chinese haze particles typically characterized by high OM (HULIS) and TMI concentrations
→ **Development of an advanced HULIS-TMI-photochemistry mechanism** based available literature data

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Multiphase mechanism development

- **Advanced photochemistry mechanism contains**
  Further multiphase formation pathways of HONO
  Iron-HULIS complex chemistry

- **Included in MCM/CAPRAM for process modelling**

$$HULIS + H_2O_{aq} \rightleftharpoons HULIS^- + H_3O^+$$
$$Fe^{2+} + HULIS^- \rightleftharpoons [Fe^{(II)}HULIS]^+$$
$$[Fe^{(II)}HULIS]^+ + O_{2(aq)} \longrightarrow [Fe^{(III)}HULIS]^{2+} + O_2^-$$
$$[Fe^{(II)}HULIS]^+ + O_2^- \longrightarrow [Fe^{(III)}HULIS]^{2+} + H_2O_{2(aq)}$$
$$+ 2\,OH^- - 2\,H_2O$$
$$[Fe^{(II)}HULIS]^+ + H_2O_{2(aq)} \longrightarrow [Fe^{(III)}HULIS]^{2+} + OH_{aq} + OH^-$$
$$[Fe^{(III)}HULIS]^{2+} + h\nu + O_{2(aq)} \longrightarrow Fe^{2+} + HULIS + HO_{2(aq)}$$

$$HO_{2(aq)} \rightleftharpoons H^+ + O_2^-$$
$$Cu^+ + HO_{2(aq)}/O_2^- \rightleftharpoons Cu^{2+} + H_2O_{2(aq)}$$
$$HSO_3^- + H_2O_{2(aq)} + H^+ \longrightarrow SO_4^{2-} + 2\,H^+ + H_2O$$

Multiphase Chemistry Mechanism
MCMv3.2 - CAPRAM 4.0α/HM2.1/AM1.0
22506 processes

Gas Phase Chemistry	Phase Transfer	Aqueous Phase Chemistry
MCMv3.2)	(Schwartz, 1986)	CAPRAM 4.0α (Chemical Aqueous Phase RAdical Mechanism)
14244 reactions	347 species	7915 reactions

Extended Fe-HULIS & HONO chemistry module
25 processes

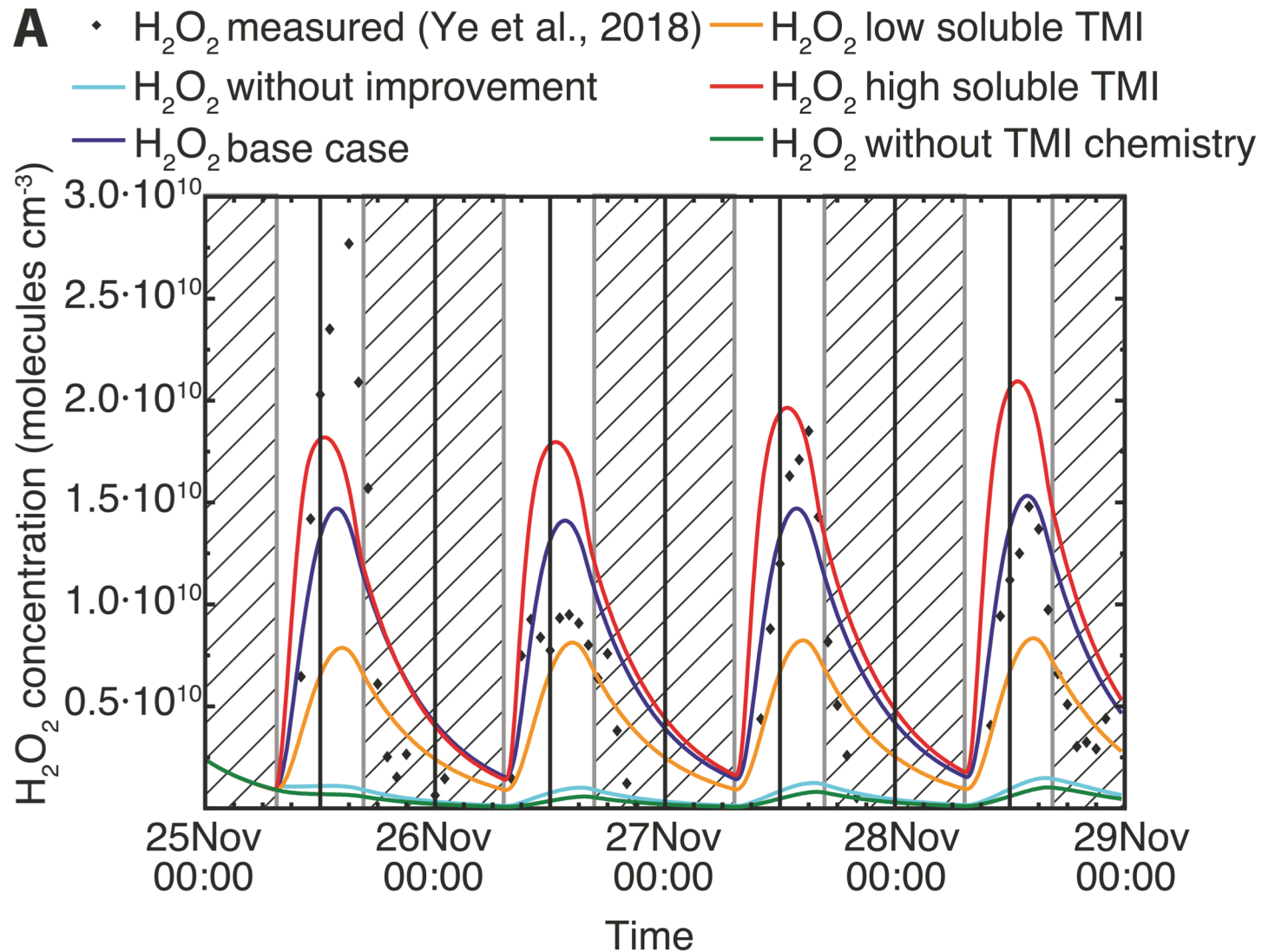|	
Gas-Phase Chemistry 6 reactions	Aqueous-Phase Chemistry 6 reactions and 7 equilibria
Phase Transfer 2 species	

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Multiphase model simulations with SPACCIM

- SPACCIM model (*Wolke et al. 2005*) simulations performed for four observation periods
- Several sensitivity runs performed examining the impact of the soluble transition metal ion (TMIs) content on the predicted H_2O_2 formation
- Model initialized mainly by observational data

Table1. Perfomed model simulations.

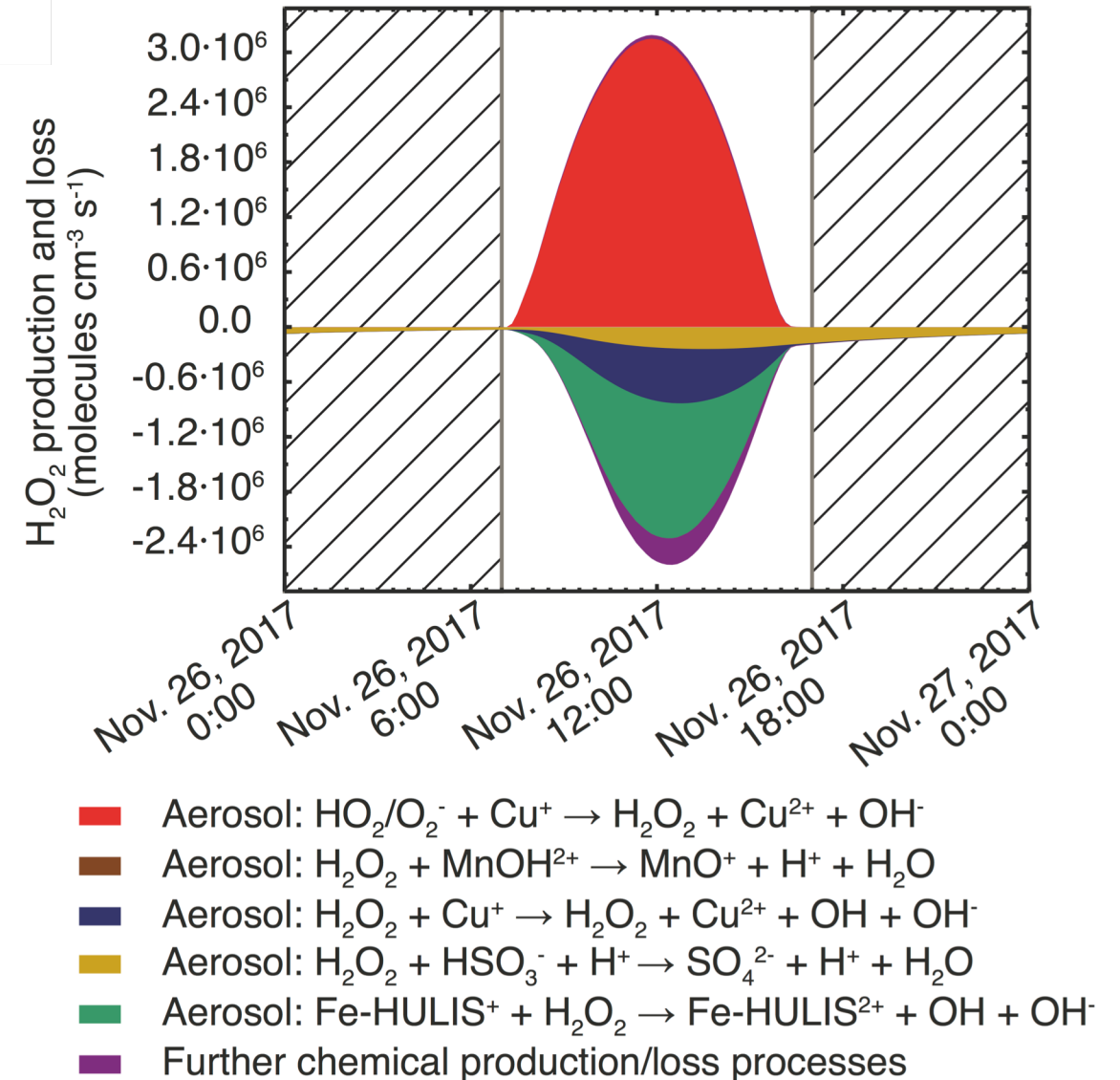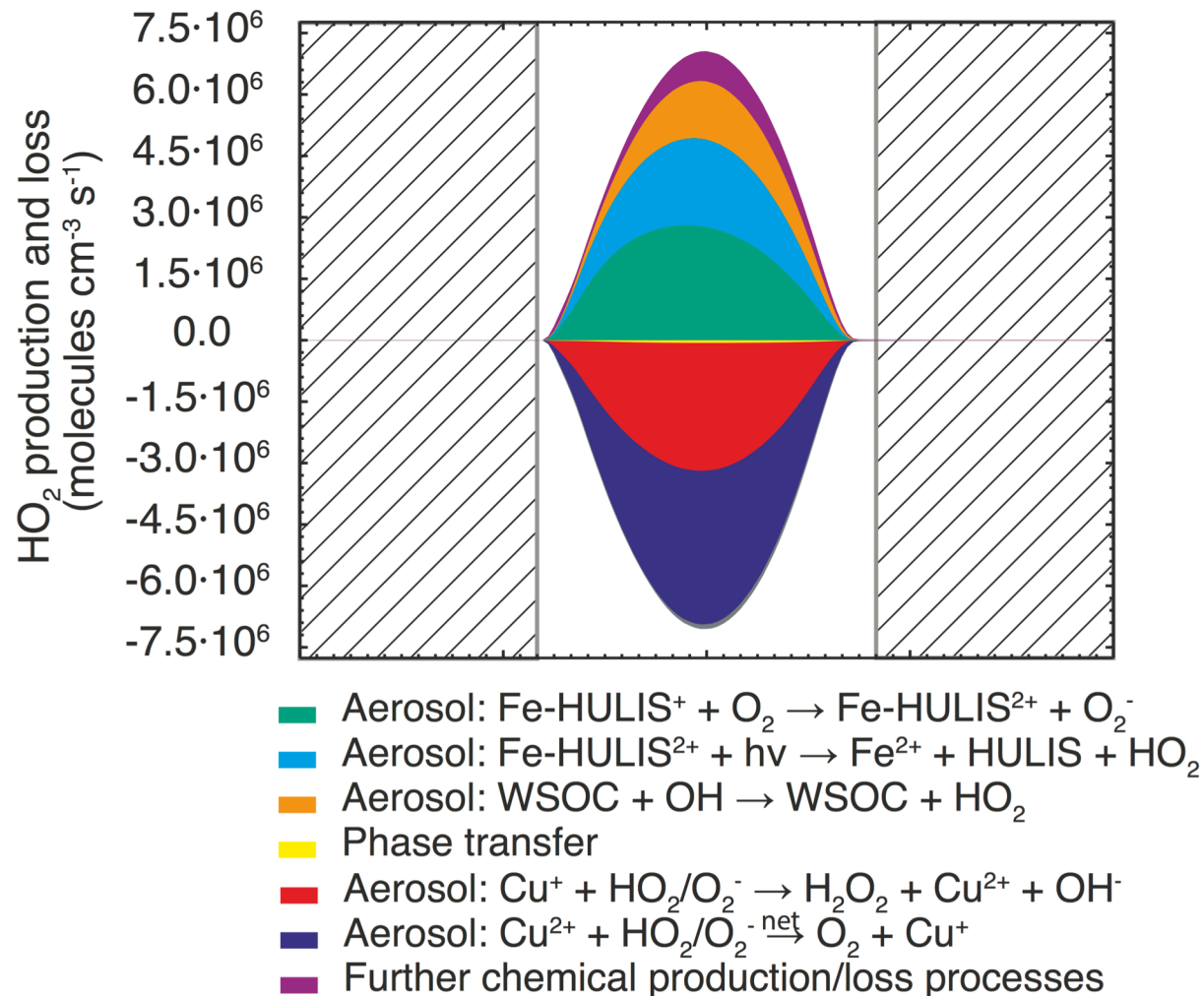| Model run	Description
without improvement	MCMv3.2–CAPRAM4.0α/ HM2.1/AM1.0
base case	MCMv3.2–CAPRAM4.0α/ HM2.1/AM1.0 with added iron-HULIS chemistry
low soluble TMI	base case with low TMI soluble fraction
high soluble TMI	base case with high TMI soluble fraction
without TMI chemistry	run without TMI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

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Modeled gas-phase H$_2$O$_2$ concentrations (2. period)

A
- · H$_2$O$_2$ measured (Ye et al., 2018)
- —— H$_2$O$_2$ without improvement
- —— H$_2$O$_2$ base case
- —— H$_2$O$_2$ low soluble TMI
- —— H$_2$O$_2$ high soluble TMI
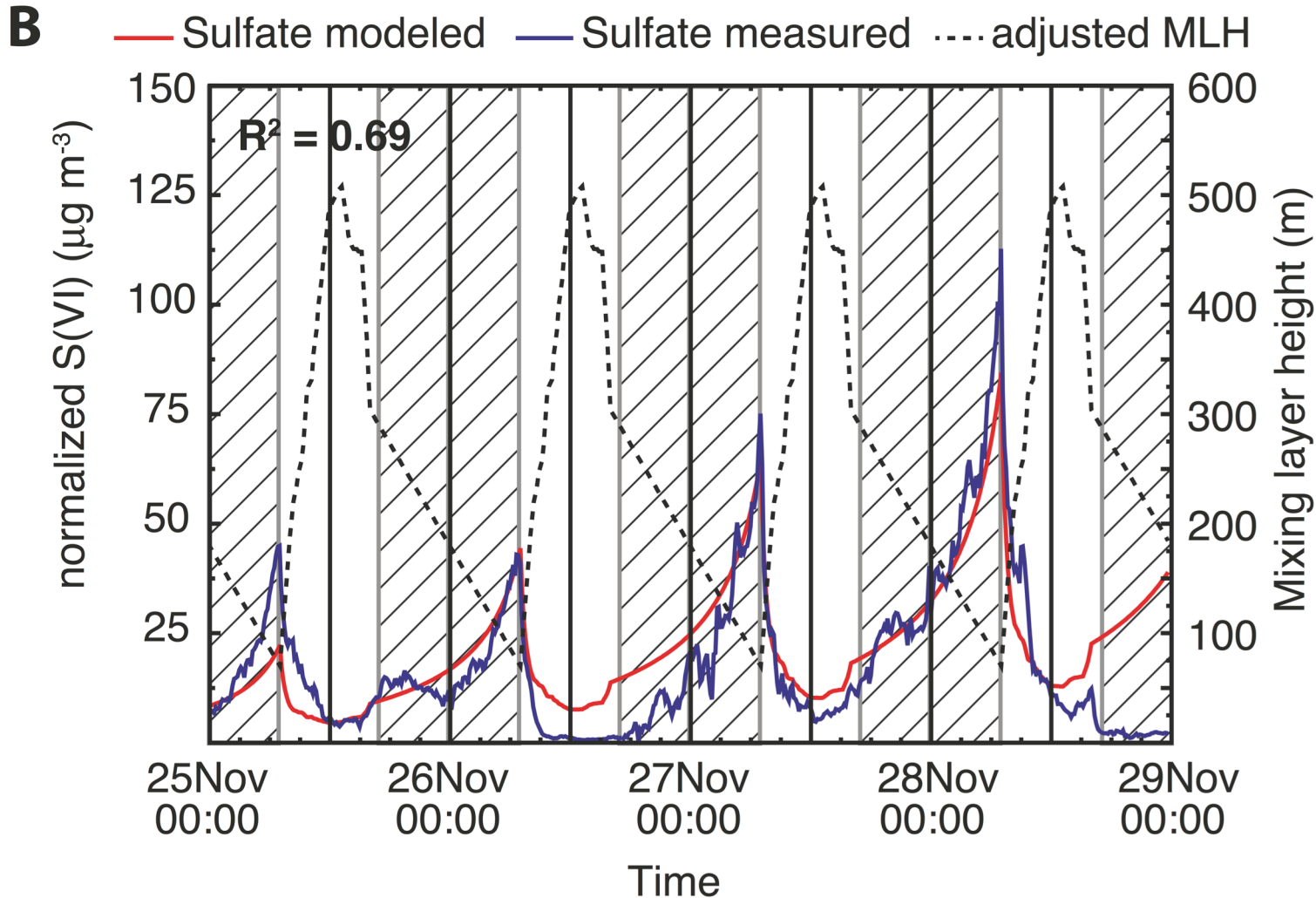- —— H$_2$O$_2$ without TMI chemistry

- Process model results
- **(i)** **Match** nicely with the **field data**
- **(ii)** **Confirm** that **H$_2$O$_2$ formation** via the new **Fe-HULIS complex** chemistry is more efficient than gas-phase HO$_2$ recombination under Chinese haze conditions
- **(iii)** **Reveal** a strong **dependency** on the **soluble metal** content

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Sources and sinks of H$_2$O$_2$ (2. period)

- Analyses of the reaction rates reveal that **H$_2$O$_2$ formation** in haze particles is result of **complex multiphase reaction sequence**.

Legend (left plot):
- Aerosol: Fe-HULIS$^+$ + O$_2$ → Fe-HULIS^{2+} + O$_2^-$
- Aerosol: Fe-HULIS^{2+} + hv → Fe^{2+} + HULIS + HO$_2$
- Aerosol: WSOC + OH → WSOC + HO$_2$
- Phase transfer
- Aerosol: Cu$^+$ + HO$_2$/O$_2^-$ → H$_2$O$_2$ + Cu^{2+} + OH$^-$
- Aerosol: Cu^{2+} + HO$_2$/O$_2^-$ $\xrightarrow{net}$ O$_2$ + Cu$^+$
- Further chemical production/loss processes

Legend (right plot):
- Aerosol: HO$_2$/O$_2^-$ + Cu$^+$ → H$_2$O$_2$ + Cu^{2+} + OH$^-$
- Aerosol: H$_2$O$_2$ + MnOH^{2+} → MnO$^+$ + H$^+$ + H$_2$O
- Aerosol: H$_2$O$_2$ + Cu$^+$ → H$_2$O$_2$ + Cu^{2+} + OH + OH$^-$
- Aerosol: H$_2$O$_2$ + HSO$_3^-$ + H$^+$ → SO$_4^{2-}$ + H$^+$ + H$_2$O
- Aerosol: Fe-HULIS$^+$ + H$_2$O$_2$ → Fe-HULIS^{2+} + OH + OH$^-$
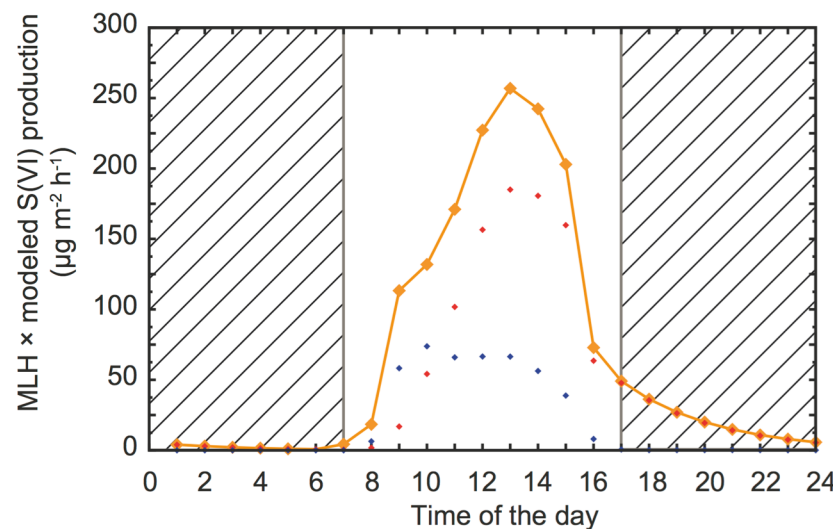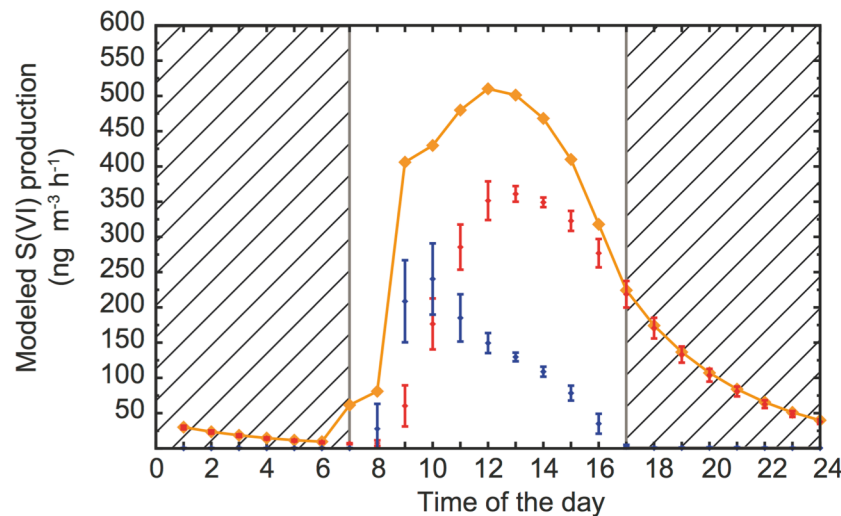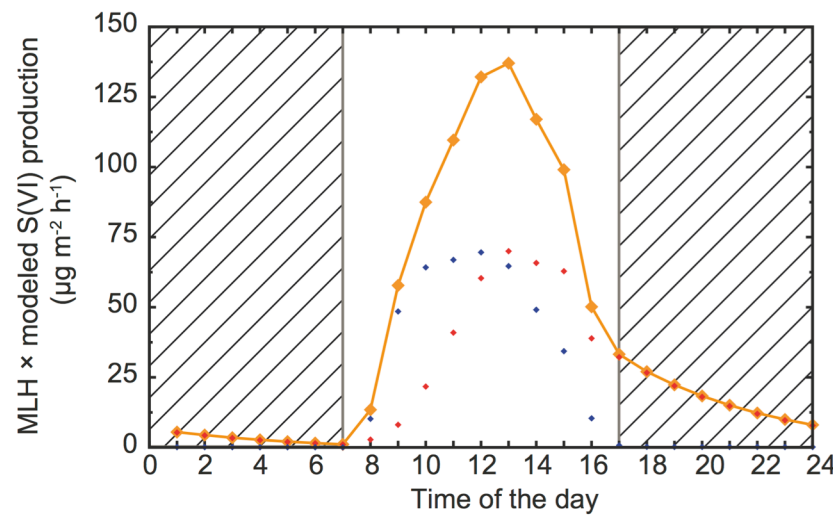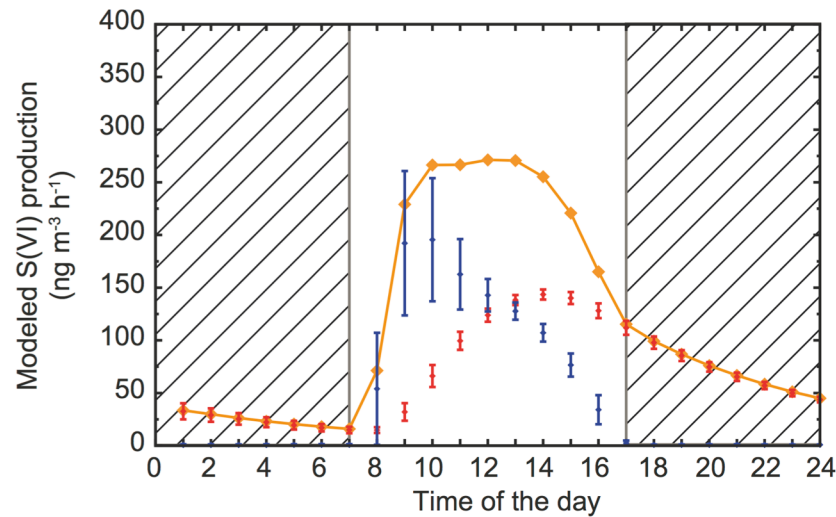- Further chemical production/loss processes

Modeled secondary S(VI) formation (2. period)

- Process **model results reveal** a quite **good agreement** in the simulated the S(IV) formation under haze conditions
- Consideration of the **mixing layer height** evolution enables a much **better interpretation** of the field observations
- **S(IV) formation** under haze conditions caused by a **complex multiphase reaction sequence**
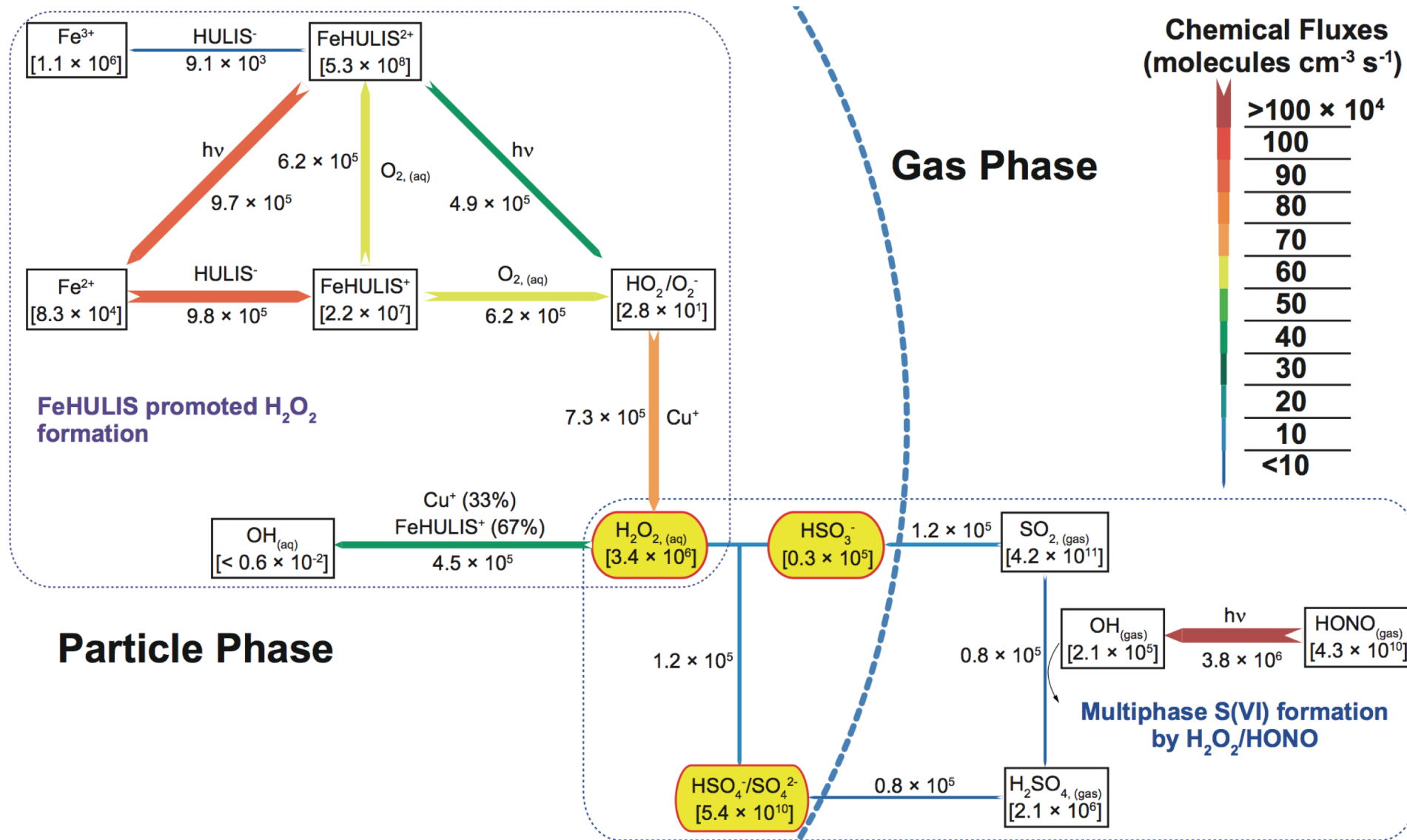
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S(VI) formation rates (2. & 3. period)

Overall S(VI) production — S(VI) production $HSO_3^- + H_2O_2$ — S(VI) production $SO_2 + OH$

- **Aqueous-phase** reaction of **H_2O_2 with S(IV)** contributes considerably to S(VI) formation **during the morning hours** besides the **HONO** related **gas-phase formation of sulfuric acid by OH**

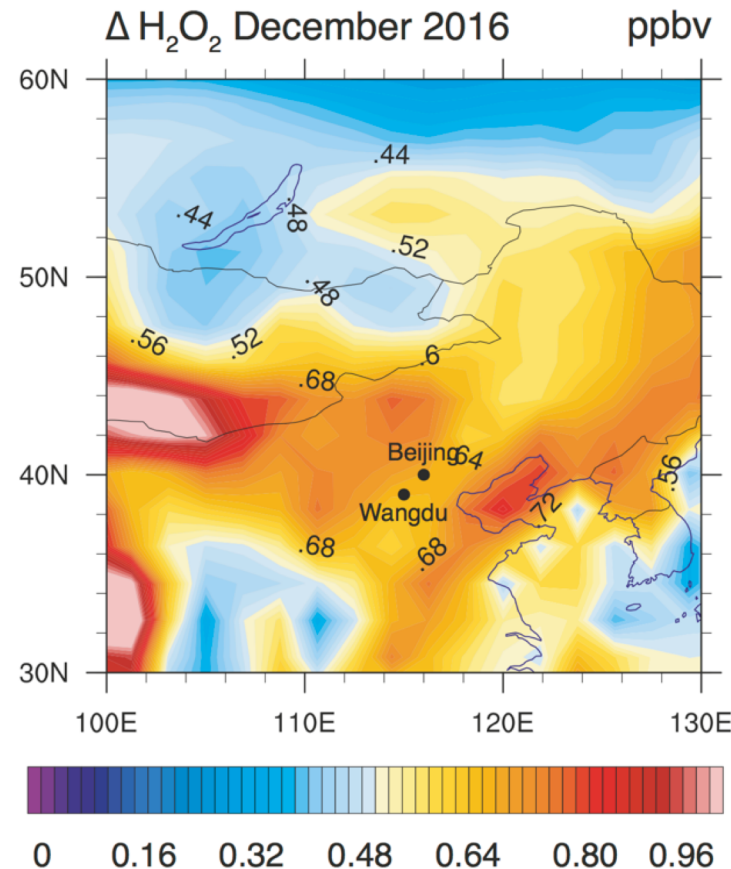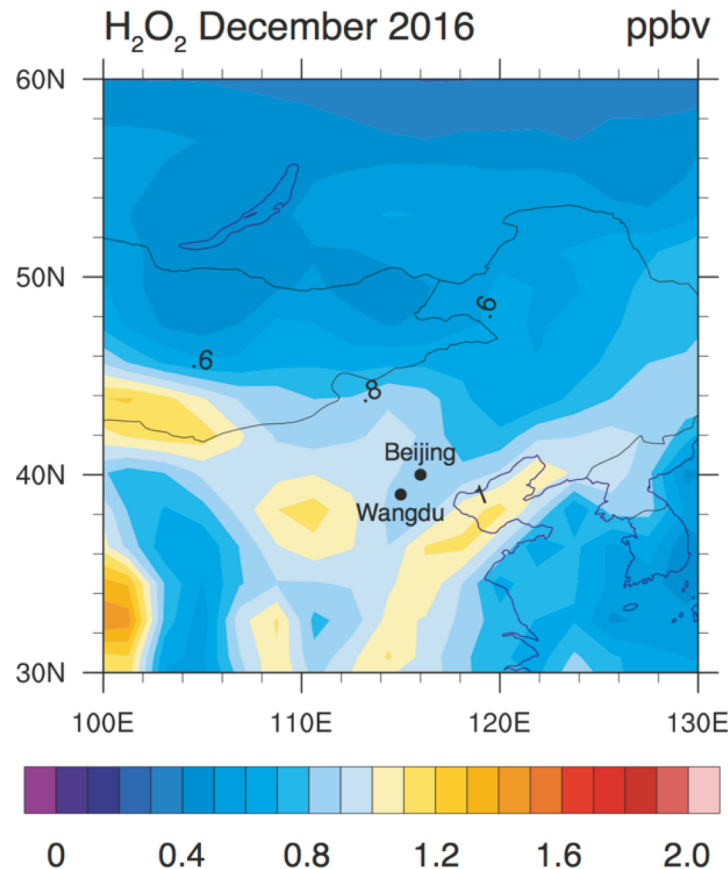# Linked aqueous H$_2$O$_2$ and multiphase S(VI) formation

- Aqueous-phase reaction of **H$_2$O$_2$ with S(IV)** contributes around $^2/_3$ to **S(VI)** formation

- **HONO** related gas-phase formation of sulfuric acid **via OH** contributes around $^1/_3$ to **S(VI)** formation

3D simulations with ECHAM-HAMMOZ

- **Parameterization** developed to study the aerosol-chemistry-promoted **H_2O_2 formation** as potential source in the model **ECHAM-HAMMOZ**

- ECHAM-HAMMOZ simulations **with** and **without parameterization** for the year **2016**
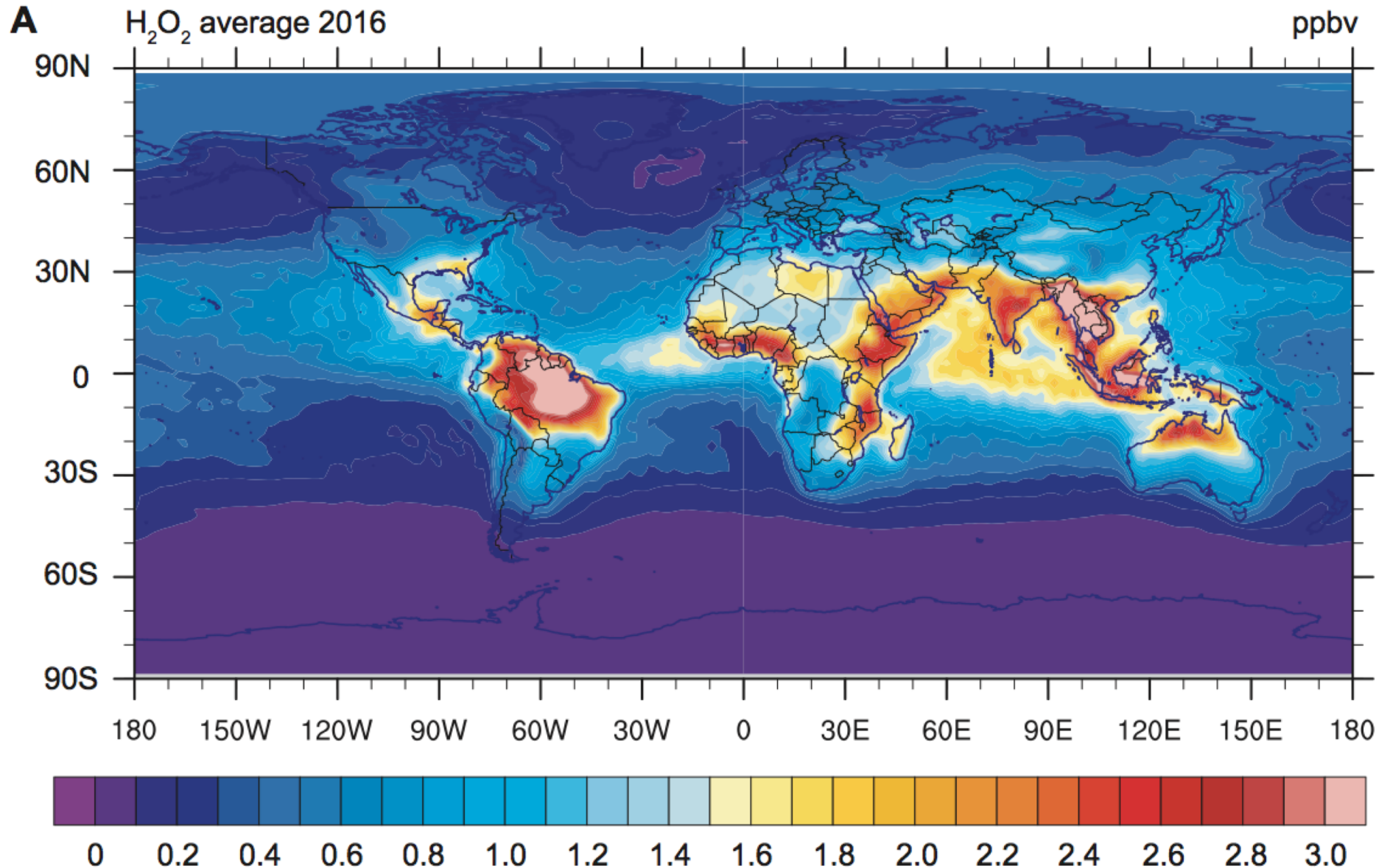

- Simulated **concentrations** in December in **better agreement** with **measurements** in the NCP
- **Significant increase** when aerosol-chemistry-promoted H_2O_2 formation considered in the model

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Summary

- Comprehensive field, chamber and model investigations performed to study potential **multiphase H_2O_2 formation** pathways under haze conditions and its **feedbacks on S(IV) oxidation and PM$_{2.5}$**

- Main findings:

(1) **H_2O_2 formed from particle-phase chemical processes** during periods with high PM$_{2.5}$ and NO_x concentrations in the North China Plain

(2) A new developed chemical mechanism explains H_2O_2 formation through a sequence of **photochemical reactions involving HULIS and TMIs**

(3) **Model can predict the unexpectedly high gas-phase H_2O_2 concentrations**

(4) **Aerosol-chemistry-promoted H_2O_2 formation** and **gas-phase HONO photolysis contributes considerably to S(VI) formation** and can explain the missing sulfate source under severe winter haze pollution conditions
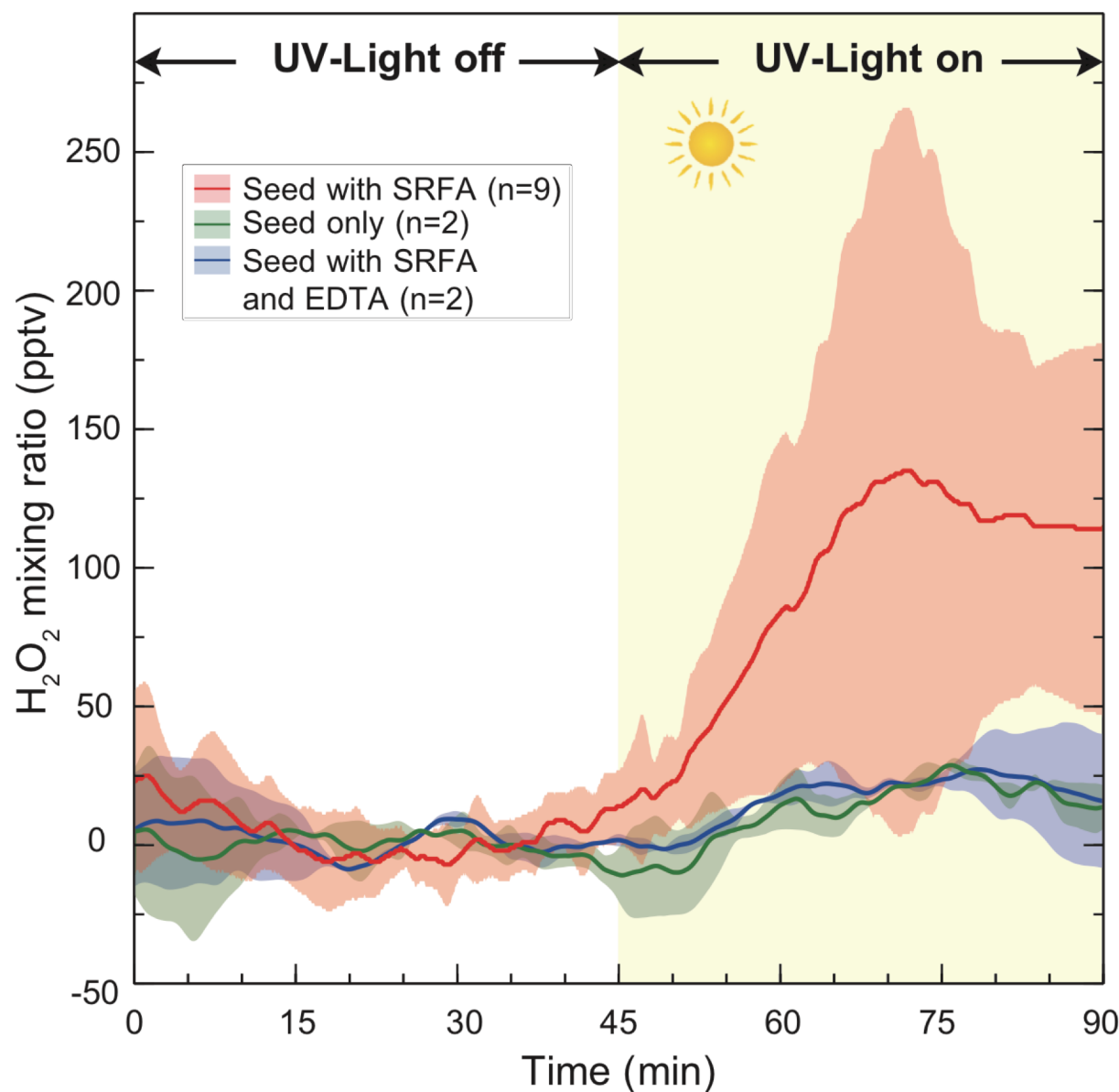
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Supplement

3D simulations with ECHAM-HAMMOZ

H$_2$O$_2$ average 2016 — ppbv

- First global model simulations show increase of gas-phase H$_2$O$_2$ by a factor of 2.8 through the newly identified particle chemistry

- Aerosol-chemistry-promoted H$_2$O$_2$ formation may an important driver for atmospheric H$_2$O$_2$

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Aerosol-chemistry-promoted H$_2$O$_2$ formation: ACD-C chamber studies

■ Aerosol-chemistry-promoted H$_2$O$_2$ formation studied for different aerosol seed compositions (with and without SRFA)

■ H$_2$O$_2$ formation observed when SRFA and UV-light present

■ Note SRFA contains also TMIs