IMPACT OF IN-CLOUD OVOC CHEMISTRY ON TROPOSPHERIC OZONE

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BACKGROUND: AQUEOUS-PHASE OZONE CHEMISTRY

In-cloud ozone mechanism

- Clouds act as ozone sink
- Main aqueous-phase sink of ozone:
  $O_3 + O_2^- \longrightarrow O_3^- + O_2$
- Aqueous-phase ozone chemistry is sensitive to HO_2 since:
  $HO_2 \rightleftharpoons O_2^- + H^+$
- Oxidation of oxygenated volatile organic compounds (OVOCs) yields HO_2 and thus enhances in-cloud ozone destruction

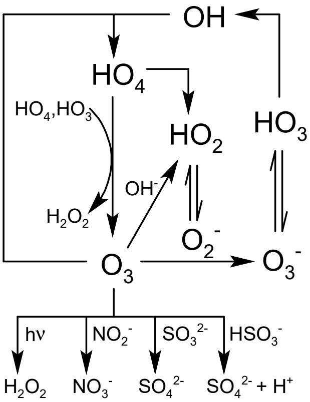


Figure 1: Graphical representation of aqueous-phase ozone chemistry.

RESEARCH OBJECTIVE

- Most global atmospheric models do not have explicit aqueous-phase chemistry (Ervens, 2015)
- The global model ECHAM/MESSy Atmospheric Chemistry (EMAC, Jöckel et al. (2010)) is capable to represent explicit in-cloud chemistry
- Using its standard aqueous-phase mechanism, EMAC estimates that $\sim$ 4 % of ozone is lost by clouds
- The standard aqueous-phase mechanism of EMAC does not include OVOC chemistry

Hypothesis

Due to the missing in-cloud oxidation of OVOCs, global models underestimate HO_2 in cloud droplets and therefore the importance of clouds as an ozone sink

Research focus

By implementing an extensive in-cloud OVOC oxidation scheme into a box-model and into EMAC, we investigate the importance of in-cloud chemistry on tropospheric ozone and the general chemical composition of the atmosphere

MECHANISM DESCRIPTION - I

Developed in-cloud OVOC mechanism

- Updated in-organic ozone chemistry (compared to standard EMAC in-cloud mechanism (Jöckel et al., 2016))
- In-cloud OVOC mechanism based on the Cloud Explicit Physico-chemical Scheme (CLEPS 1.0, Mouchel-Vallon et al. (2017))
- Modifications compared to CLEPS:
  - Selection of OVOCs containing 1-4 carbon atoms (34 species, 304 reactions)
  - Explicit simulation of hydration and dehydration of carbonyl compounds
  - Hydrolysis of peroxy acetyl radical (precursor of PAN)
  - Gas-phase oxidation of outgassed gem-diols (RC(OH)(OH)) and oxalic acid
  - Oligomerisation of formaldehyde, glyoxal, and methylglyoxal
  - More detailed photolysis chemistry
  - Optimisation for global model application

MECHANISM DESCRIPTION - II

Example: Glyoxal

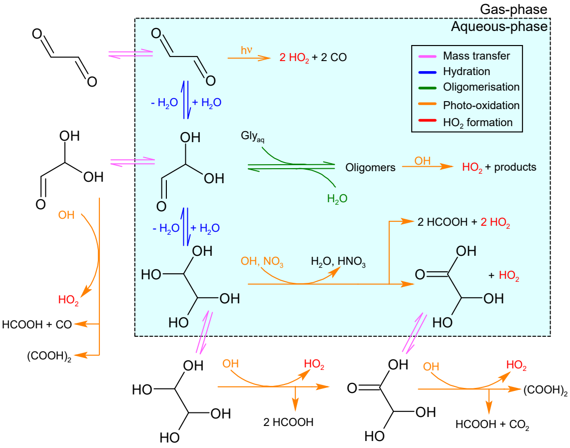


Figure 2: Representation of the newly introduced mechanism using glyoxal as an example.

MODELLING APPROACH

Box-model and global model description

- Three different in-cloud mechanisms are modelled (same colours are used in figures)
  - Minimum: Includes the uptake of a few soluble compounds, their acid based equilibria and the oxidation of SO_2 via O_3 and H_2O_2 (Jöckel et al., 2006). Considered to represent the capabilities of most global models (Ervens, 2015).
  - Standard: Includes an advanced aqueous-phase mechanism, representing more than 150 reactions (Jöckel et al., 2016)
  - New: Complex OVOC oxidation mechanism developed in this study
- Box-model: Chemistry As A Boxmodel Application (CAABA, Sander et al. (2019))
  - Represents an air-parcel at mid-latitude with a temperature of 278 K and a humidity of 70 %
  - Cloud event between 12 and 13 UTC with a droplet radius of 20 µm and a liquid water content of 0.3 g/L. At 13 UTC the cloud evaporates and all species are outgassed.
- Global model: ECHAM/MESSy Atmospheric Chemistry (EMAC, Jöckel et al. (2010))
  - Resolution: T63L90MA (1.875 by 1.875 degrees in latitude and longitude, 90 levels)
  - 2014 as spin-up, 2015 for analysis
  - Nudged simulation using ERA-Interim data
  - Gas-phase mechanism: Mainz Organic Mechanism (MOM, Sander et al. (2019))

BOX-MODEL RESULTS - I

Box-model results with a cloud event between 12 and 13 UTC

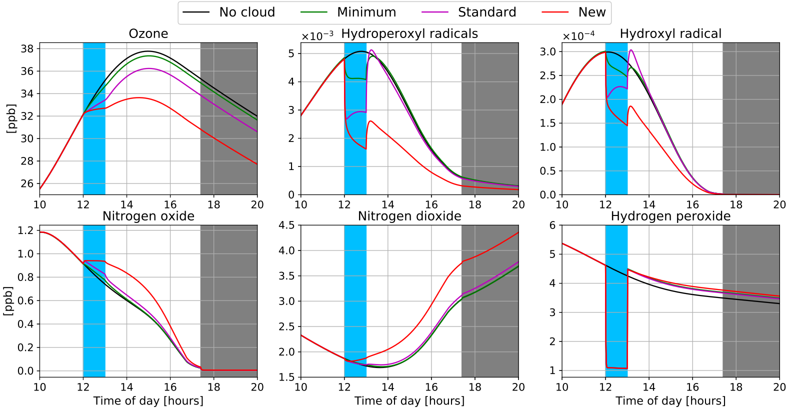


Figure 3: Box-model results for a selection of species with a cloud event between 12 and 13 UTC (blue shading). Night-time indicated by grey background shading.

BOX-MODEL RESULTS - II

Box-model results with a cloud event between 12 and 13 UTC

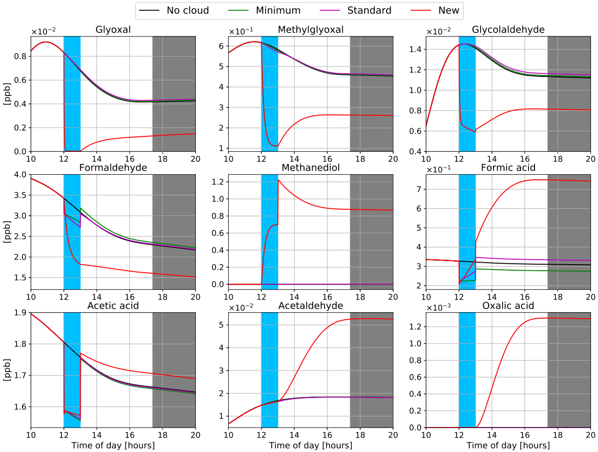
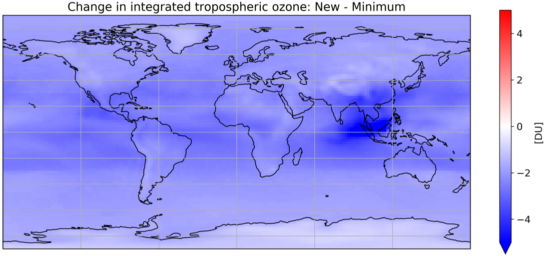
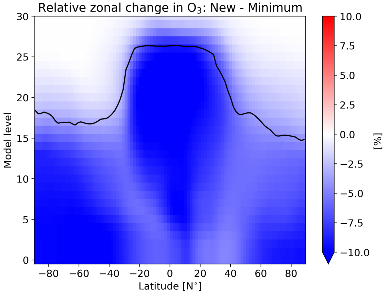


Figure 4: Box-model results for a selection of species with a cloud event between 12 and 13 UTC (blue shading). Night-time indicated by grey background shading.

GLOBAL MODEL RESULTS - IMPACT ON OZONE - I

Changes in tropospheric ozone columns on 30 September





- Both the standard and the developed OVOC mechanism lead to a reduction of tropospheric ozone. The changes induced by the new OVOC mechanism is significantly higher (3 DU may accounts for more than 10 % of the total column).
- Due to the ongoing Indian monsoon, ozone is efficiently removed by scavenging, leading to a reduction in tropospheric ozone in this area

GLOBAL MODEL RESULTS - IMPACT ON OZONE - II

Yearly tropospheric odd oxygen[1] budget

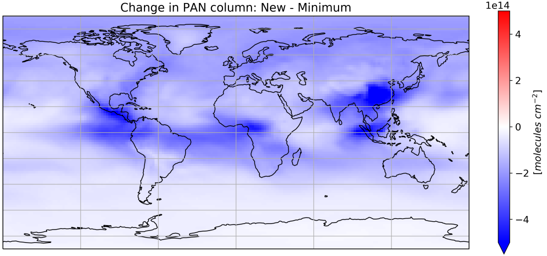
	Unit	Minimum	Standard	New
Sources				
Chemical production	Tg/a	5895.6	5902.7	5739.8
STE[2]	Tg/a	355.2	360.8	370.5
Sinks				
Chemical loss	Tg/a	5254.7	5163.5	4831.5
Dry deposition	Tg/a	846.5	837.4	799.2
Wet deposition	Tg/a	0.1	0.1	0.1
Scavenging	Tg/a	149.7	262.6	479.4
Of which O_3	%	8.8	44.6	70.1
O_3 **burden**	Tg	349	344	324
O_3 **lifetime**	days	20.3	20.0	19.3

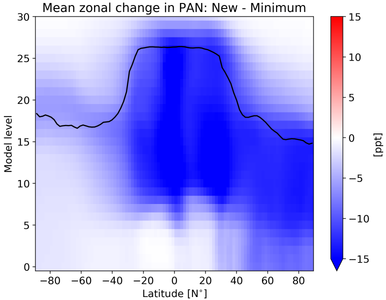
[1]Odd oxygen is defined as: $O_x \equiv O + O_3 + NO_2 + 2 \times NO_3 + 3 \times N_2O_5 + HNO_3 + HNO_4 + ClO + HOCl + ClNO_2 + ClNO_3 + BrO + HOBr + BrNO_2 + 2 \times BrNO_3 + PANs + PNs$ to account for rapid cycling between O_x species

[2]Stratospheric-Tropospheric Exchange

GLOBAL MODEL RESULTS - IMPACT ON PAN

Changes in tropospheric PAN columns on 30 September





- Many precursors of PAN are efficiently removed by scavenging
- The missing PAN precursors in the gas-phase reduce the formation of PAN
- Efficient removal of PAN precursors during the Indian monsoon leads to a reduction of PAN in the effected area

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CONCLUSIONS

Summary:

- With the newly developed extensive in-cloud OVOC oxidation scheme the importance of ozone scavenging increases from 2.4 % (Minimum) to 7.8 % (New)
- The findings in this study show that models, neglecting explicit complex in-cloud chemistry, underestimate clouds as an ozone sink
- The new in-cloud mechanism reduces the bias of EMAC towards high tropospheric ozone (Jöckel et al., 2016)
- Due to the uptake of PAN precursors, tropospheric PAN is reduced

Outlook:

- Quantify the reduction of EMAC's bias towards high tropospheric ozone
- Detailed comparisons of modelled data with observations
    - Satellite observations: IASI-FORLI
    - Airborne flight campaigns: IAGOS, OMO

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