New Tagging

J. Coates[1] and T. Butler[1]

[1]Institute for Advanced Sustainability Studies, Potsdam, Germany

August 3, 2015

Abstract

1 Introduction

2 Methodology

2.1 VOC Tagging Approach

- boxmodel set-up, initial conditions, VOC emissions same as in Coates and Butler (2015)
- only difference is the tagging approach used; Coates and Butler (2015) determine effects of VOC on O3 by inferring the effects of VOC on Ox production, hence this is looking at the effects on O3 indirectly
- the tagging approach of Emmons et al. (2012), which looks at NOx-tagging has been adapted to VOC tagging by Shuai and Tim and now the effects of VOC on O3 mixing ratios can be directly compared
- Tagging the VOC degradation of MOZART-4 was achieved using the same technique as S&T but using the KPP version of MOZART-4, including the modifications to MOZART-4 outlined in Coates and Butler (2015) such as using MCM v3.2 inorganic chemistry, using only reactions relevant to tropospheric processes.
- From the gas-phase reactions in the KPP version, we have the full set of non-tagged reactions – the "real" chemistry – and appended this with reactions where the degradation reactions

of a VOC are tagged for the VOC in order to trace the effects of the VOC degradation on O3 and Ox production.

- The tagging approach requires extracting the set of reactions where reactions of the VOC products with members of the Ox family are also included.
- We define the Ox family to include O3, O, O1D, NO2, NO3, N2O5, HNO3, ISOPNO3, ONIT, ONITR, HO2, HO2NO2.
- The set of tagged chemistry which runs parallel to the "real" chemistry was then added to the KPP version of MOZART-4 chemical mechanism described above.
- This chemistry was then implemented in the boxmodel and then tested to determine that the tagged chemistry does not influence the "real" chemistry by comparing the mixing ratios of tagged species to their non-tagged counterparts. If the chemistry is correctly set-up then there should be no difference.
- The next testing stage was that this new chemistry set-up gives the same results as the previous chemistry (i.e. the results in Coates and Butler (2015)) by comparing the mixing ratios of the "real" chemistry in the new set-up to that in Coates and Butler (2015) and again there should be no differences as the boxmodels are set-up in exactly the same way.
- The final boxmodel setup was used as the base case for each of the subsequent modelling scenarios, and simulates NOx conditions that produce maximum ozone for each VOC.

2.2 Vertical Mixing with Diurnal Boundary Layer Height

- The base boxmodel (Sect. 2.1) includes a constant boundary layer height of 1 km and no interactions (mixing) with the free troposphere.
- A parameterisation of the diurnal profile of the planetary boundary layer (PBL) height over Los Angeles was provided by Boris Bonn based on data from the CARES field campaign (CARB, 2008) .
- The PBL height was calculated at every time point for the model run and then read into the boxmodel at each time point .
- The concentrations of the chemical species within the PBL are diluted due to the larger mixing volume when the PBL height increases at the beginning of the day, also the increasing

check if reference correctly

include plot

PBL height induces mixing of chemical species from the free troposphere with those chemical species within the PBL i.e. vertical mixing. When the PBL height collapses during night giving the stable nocturnal boundary layer, this traps the chemical species into a smaller volume thus increasing the concentrations of the chemical species.

- This vertical mixing scheme was implemented into the boxmodel using the same approach of Lourens (2012).

- The mixing ratios of O3, CO and CH4 in the free troposphere were respectively set to 50 ppbv, 116 ppbv and 1.8 ppmv. These condions were taken from the MATCH-MPIC chemical weather forecast model on the 27th March (the start date of the simulations). The model results (`http://cwf.iass-potsdam.de/`) at the 700 hPa height were chosen and the daily average was used as input into the boxmodel.

- Tagged free troposphere species were also included in the boxmodel to determine effect of free troposphere species on surface ozone levels.

check about reference and if this is appropriate

2.3 Low and High NOx Conditions

- The NOx conditions in the base boxmodel (Sect. 2.1) represent an idealised case in which NOx-VOC-sensitive chemistry is held throughout the simulation. In reality, NOx conditions may give rise to NOx-sensitive (low NOx) or VOC-sensitive (high NOx) in which the maximum potential of a VOC may not be reached.

- We have scaled the NO emissions calculated for NOx-VOC-sensitive chemistry by a factor of 0.5 for the low NOx model run and by 1.5 for the high NOx model run.

confirm sensitivity with NOx

2.4 Increased Temperature

- The base boxmodel run (Sect. 2.1) uses a constant temperature of 293 K (20∘C). In the future, the global temperature is extremely likely to increase and as highlighted by the review of Pusede et al. (2015), this tends to lead to increased surface level ozone.

- Pusede et al. (2015) highlight that an increase in temperature driven emissions will be the main driver in increased ozone levels in the future, other drivers are chemical in nature and the role of alkyl nitrate chemistry is thought to play a role in increasing ozone levels. The chemistry of alkyl nitrates is thought not to be well-represented in chemical mechanisms

used in chemical transport models, hence models are unable to simulate the increased ozone levels produced by temperature dependant alkyl nitrate chemistry.

- While the set-up of our boxmodel does not allow us to study the importance of tropospheric ozone production to temperature dependent emissions, our set-up does allow us to verify how the effects of the representation of alkyl nitrate chemistry influence ozone production.

- We run the base boxmodel set-up at an increased temperature of 295 K (22∘C) to compare the ozone production under different temperature scenarios.

3 Results

4 Conclusions

References

CARB. 2010 CalNex White Paper: Research at the Nexus of Air Quality and Climate Change. Technical report, California Air Resources Board, 2008.

J. Coates and T. M. Butler. A comparison of chemical mechanisms using Tagged Ozone Production Potential (TOPP) analysis. *Atmospheric Chemistry and Physics Discussions*, 15(8):12389–12422, 2015.

L. K. Emmons, P. G. Hess, J.-F. Lamarque, and G. G. Pfister. Tagged ozone mechanism for MOZART-4, CAM-chem and other chemical transport models. *Geoscientific Model Development*, 5:1531–1542, 2012.

AsM Lourens. *Air quality in the Johannesburg-Pretoria megacity: its regional influence and identification of parameters that could mitigate pollution.* PhD thesis, North-West University, Potchefstroom Campus, 2012.

Sally E. Pusede, Allison L. Steiner, and Ronald C. Cohen. Temperature and recent trends in the chemistry of continental surface ozone. *Chemical Reviews*, 115(10):3898–3918, 2015.