

Impact of C₁-C₅ alkyl nitrate chemistry on tropospheric ozone - a box modelling study

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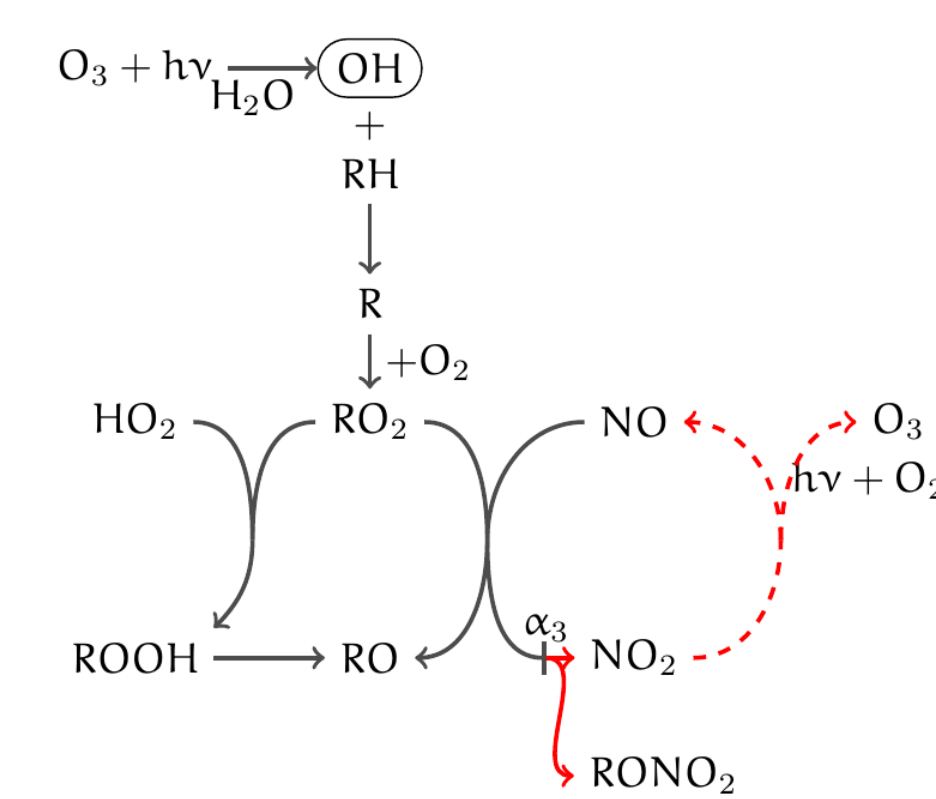
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1 Introduction

Alkyl nitrates (RONO₂) are a group of organic trace gases that are present in the atmosphere as a result of direct emissions and secondary photochemical production from the oxidation of hydrocarbons in the presence of nitrogen oxide (NO). Their formation terminates the tropospheric ozone (O₃) production by temporarily storing the active form of nitrogen. Due to a relatively long lifetime of a few days to a few months, RONO₂ can be destroyed far away their sources by photolysis or hydroxyl radical (OH) oxidation, releasing nitrogen dioxide (NO₂) to the local atmosphere. This might influence O₃ concentrations on regional levels and alter the oxidative capacity of the atmosphere.



In spite of their importance, there are few studies that investigate the impact of RONO₂ chemistry on tropospheric O₃ using a global chemistry-climate model. Here we extend the tropospheric chemical mechanism (CheT) of the United Kingdom Chemistry and Aerosols (UKCA) model to include the chemistry of C₄-C₅ alkanes (RH) and C₂-C₅ RONO₂.

Before implementation, we test the new mechanism in a box model in a range of NO_x-RH conditions using the Master Chemical Mechanism (MCM) as a benchmark and evaluate the impact of C₁-C₅ RONO₂ on O₃.

2 Box model setup

Two types of box model simulations are performed.

2.1 Steady state

• “Steady state” simulations are run until a steady state O₃ concentration is reached. It is accomplished by keeping concentrations of the species driving O₃ chemistry, NO_x and RH, constant in time.

• The mechanisms are compared in the NO_x-RH chemical space using isopleth plots of 24 hour average concentrations of species of interest.

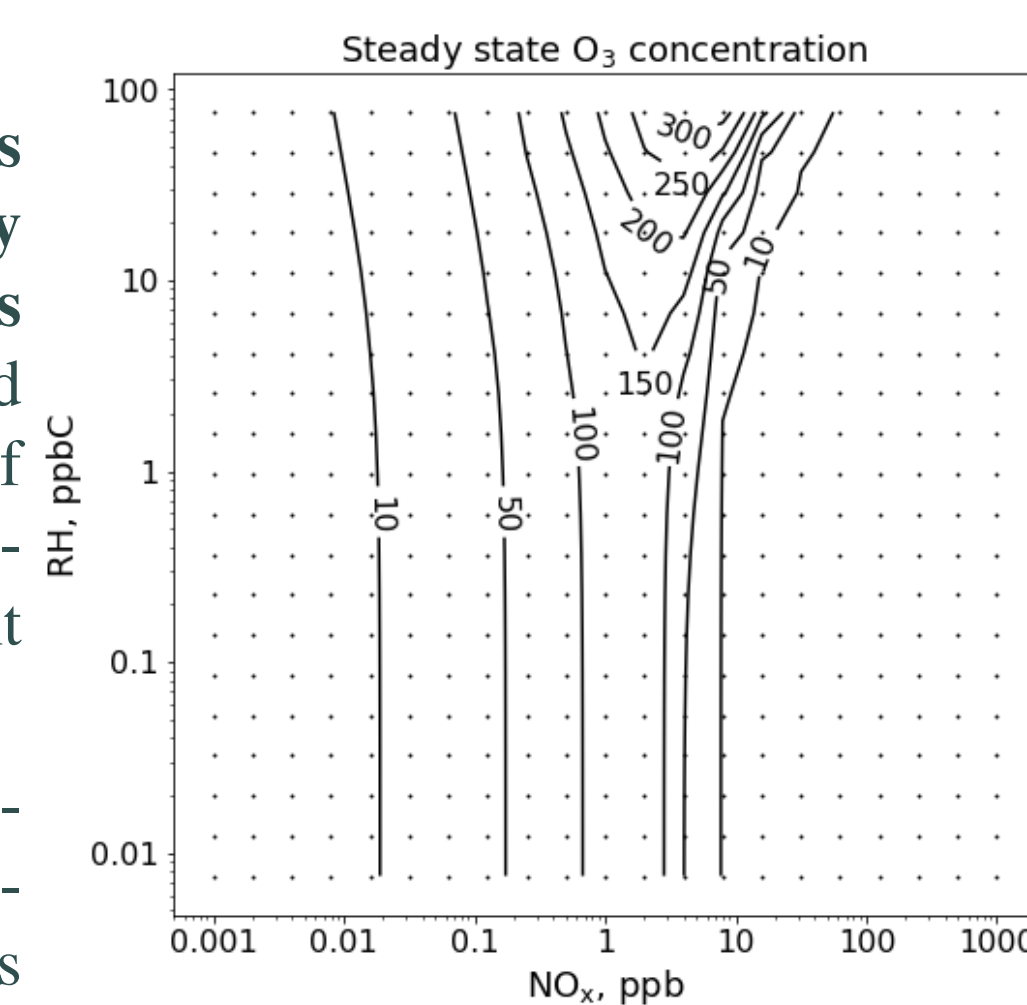


Figure 1: Isopleths of O₃ steady state concentrations. Dots show individual box model runs.

Initialised variable species	O ₃ , NO
Fixed species*	CO, C ₁ -C ₅ alkanes
Emissions	NO, NO ₂ at a ratio computed online
Deposition	O ₃ , H ₂ O ₂ , HNO ₃

*Apart from N₂, O₂ and H₂O

2.2 Initial pulse

• “Initial pulse” simulations imitate air being transported away from an emission source and evolving purely due to chemical interactions.

• Initialised variable species: O₃, NO, CO, C₁-C₅ alkanes.

3 Updating the CheT inorganic and C₁-C₃ alkane chemistry

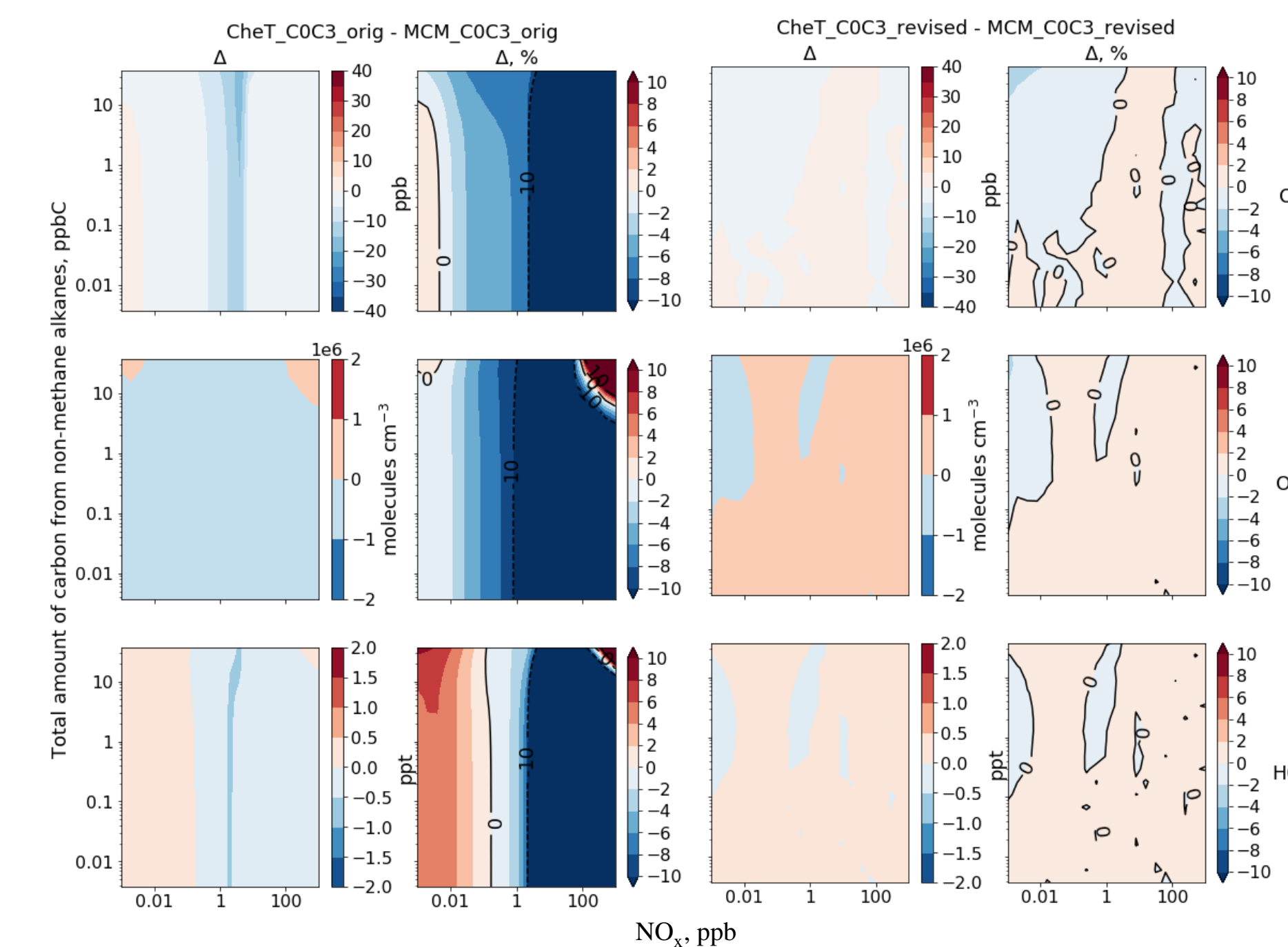


Figure 2: Differences between steady state runs with the MCM and CheT inorganic and C₁-C₃ RH chemistry before (two left columns) and after (two right columns) revision.

- The original CheT mechanism includes representation of the inorganic, C₁-C₃ RH and isoprene chemistry. For simplicity, the latter is excluded from the CheT here.
- Before adding new chemistry to the CheT, we suppress differences between the original CheT and an analogous subset from the MCM by unifying and updating reaction rate coefficients.

4 Adding C₄-C₅ alkane chemistry

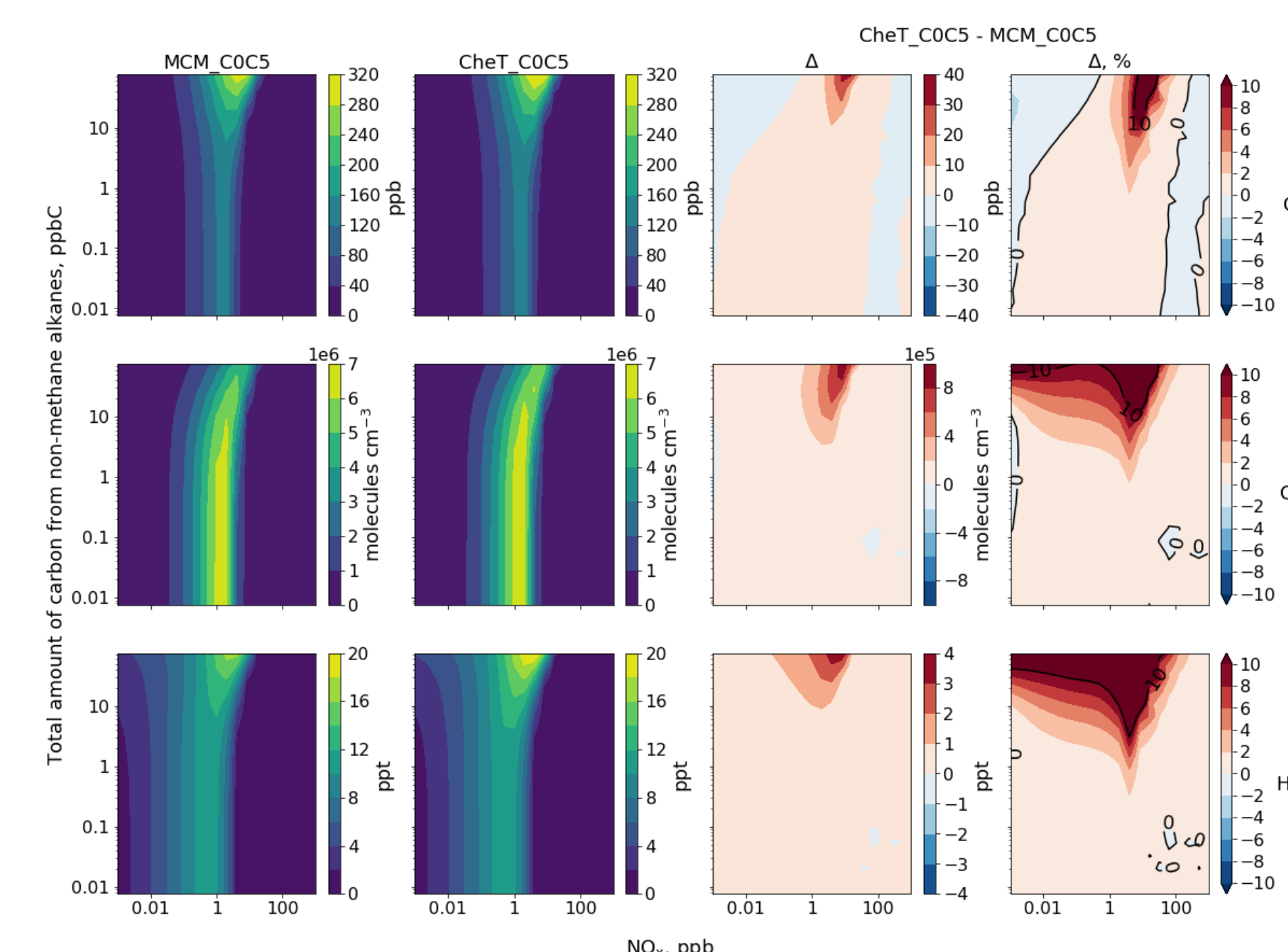


Figure 3: Differences in O₃, OH and HO₂ between steady state runs with the MCM and CheT inorganic and C₁-C₅ RH chemistry.

- Proposed version of the C₄-C₅ alkane chemistry requires addition of 20 species and 58 reactions. They describe the formation of peroxy radicals from alkane oxidation by OH, their secondary production from peroxides and interactions with NO and NO₃. No new aldehydes or ketones are included.
- O₃, OH and HO₂ concentrations are now overestimated by the CheT in the mid-range NO_x and high RH conditions.

5 Impact of C₁-C₅ alkyl nitrate chemistry

5.1 Steady state

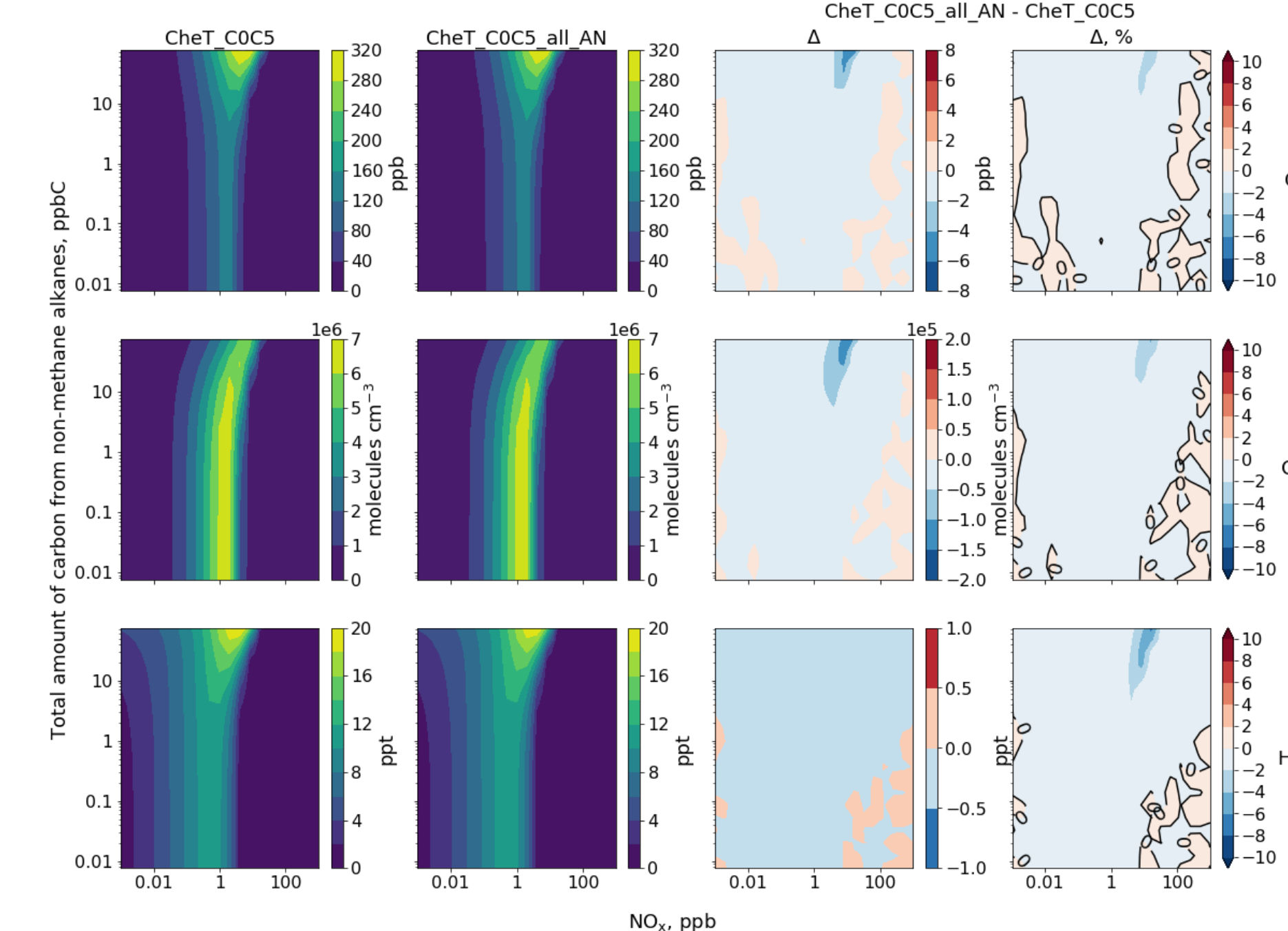


Figure 4: Differences in O₃, OH and HO₂ between CheT steady state runs with and without C₁-C₅ RONO₂ chemistry.

- Methyl (C₁) nitrate is present in the original CheT mechanism. Its chemistry is excluded from the analysis in sections 3 and 4, but is included here.
- Proposed version of the C₂-C₅ alkyl nitrate chemistry requires addition of 11 species, 33 new reactions and modification of 3 original reactions. They describe RONO₂ formation and destruction by photolysis and OH oxidation.
- Inclusion of the C₁-C₅ alkyl nitrate chemistry lowers O₃, OH and HO₂ concentrations by 2% in the majority of NO_x-RH conditions in a box model.
- Reduction is slightly bigger in a number of runs with mid-range NO_x and high RH, where the highest ozone concentrations are generated.

Conclusion: C₁-C₅ RONO₂ chemistry lowers steady state O₃, OH and HO₂ concentrations by 2% in almost all NO_x-RH conditions examined in a box model.

Forthcoming research

- Implement proposed here version of C₄-C₅ RH and C₂-C₅ RONO₂ chemistry into the UKCA.
- Run UKCA with and without RONO₂ for 10 years.
- Compare modelling results with observational data using ratios of RONO₂ to their parent alkanes as a metric.
- Evaluate differences in O₃, HO_x and NO_x burdens and distribution.

5.2 Initial pulse

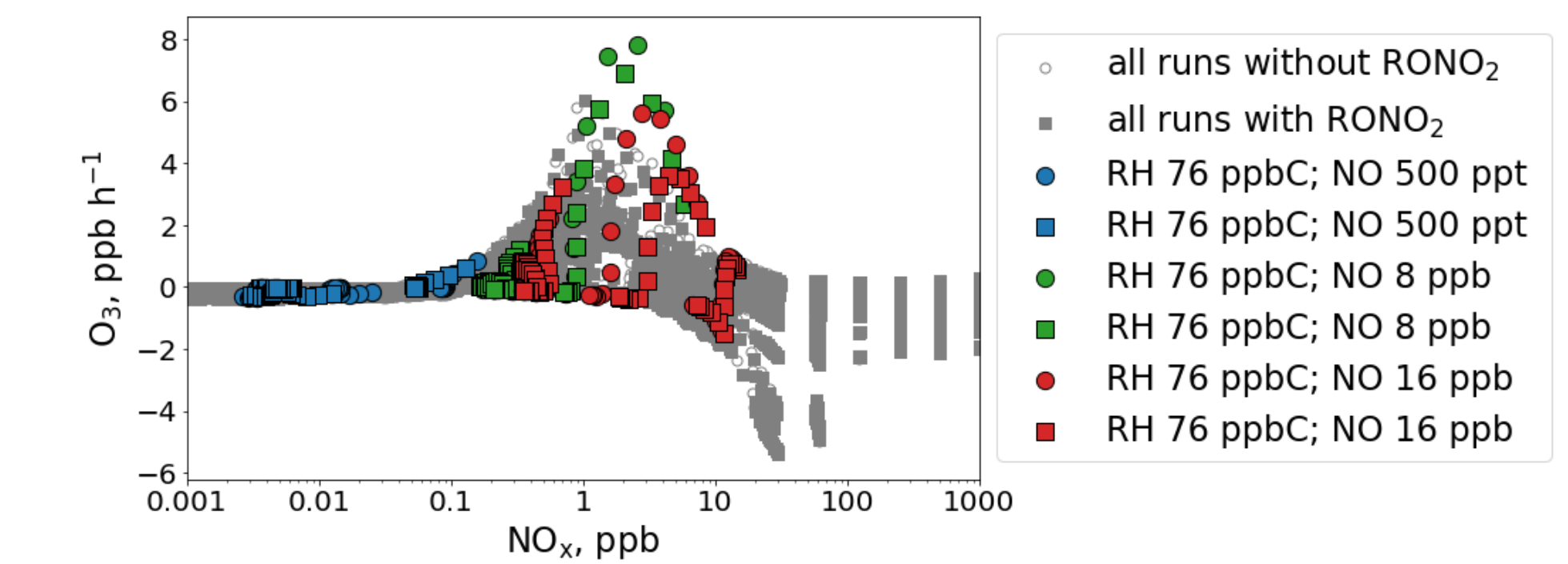


Figure 5: O₃ production in initial pulse runs with the extended CheT mechanism.

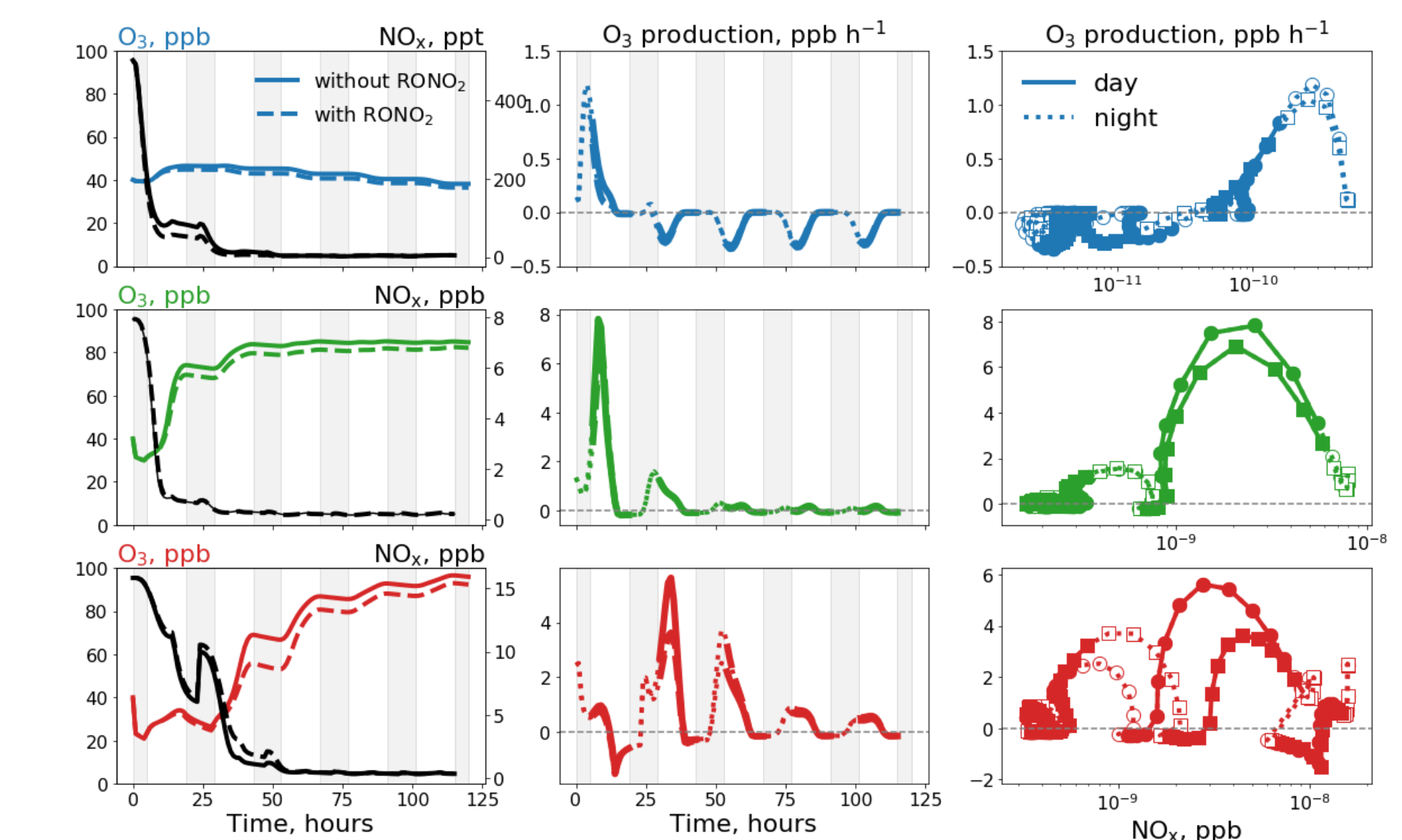
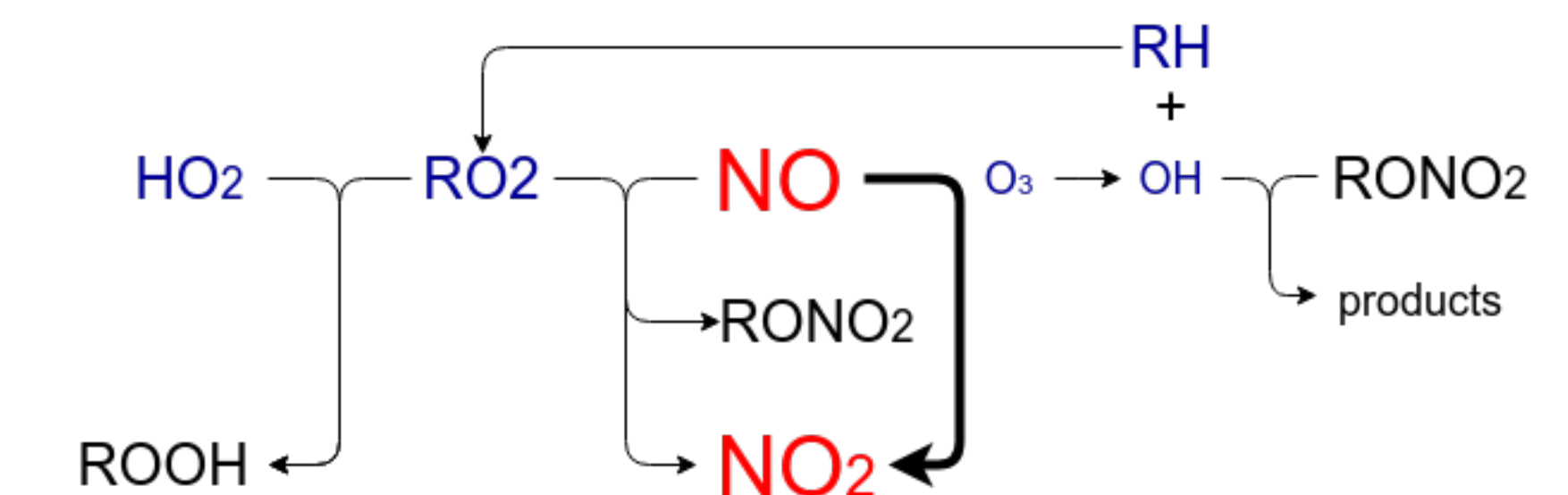


Figure 6: O₃ and NO_x mixing ratios (left column) and O₃ production (middle and right column) in the runs highlighted in Figure 5.



- In O₃ production regime, slower NO consumption due to inclusion of RONO₂ chemistry results in higher NO concentration that triggers a more effective NO titration during the day.
- Maximum contribution of ∑RONO₂ production and loss to other fluxes in all NO_x-RH conditions simulated with the extended CheT mechanism in a box model:
 - OH (<0.5%) and NO (<4%) loss;
 - HO₂ (<0.5%) and NO₂ (up to ≈5%) production;
 - RO₂ recycling (production <1.5%, loss up to ≈5%).

Conclusion: C₁-C₅ RONO₂ chemistry slows down NO to NO₂ conversion after initial burst of pollution and leads to smaller O₃ concentrations in all NO_x-RH conditions examined in a box model.

Acknowledgements. The authors thank the Natural Environment Research Council for funding the OXBUDS project and Lord Zuckerman for PhD research studentship.