Impact of alkyl nitrate chemistry on tropospheric ozone

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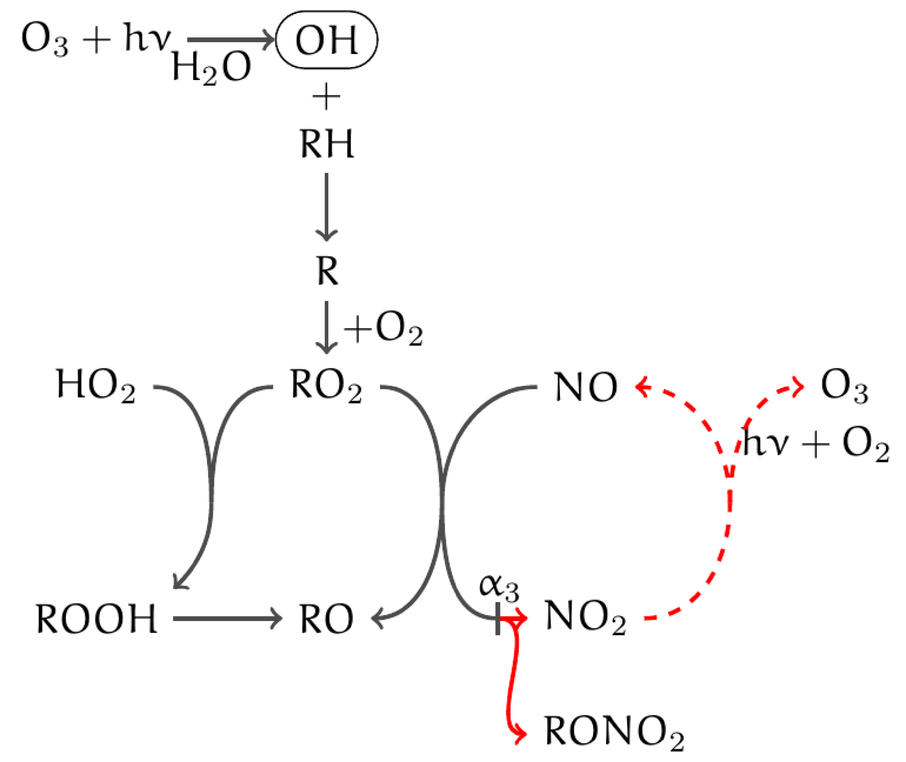
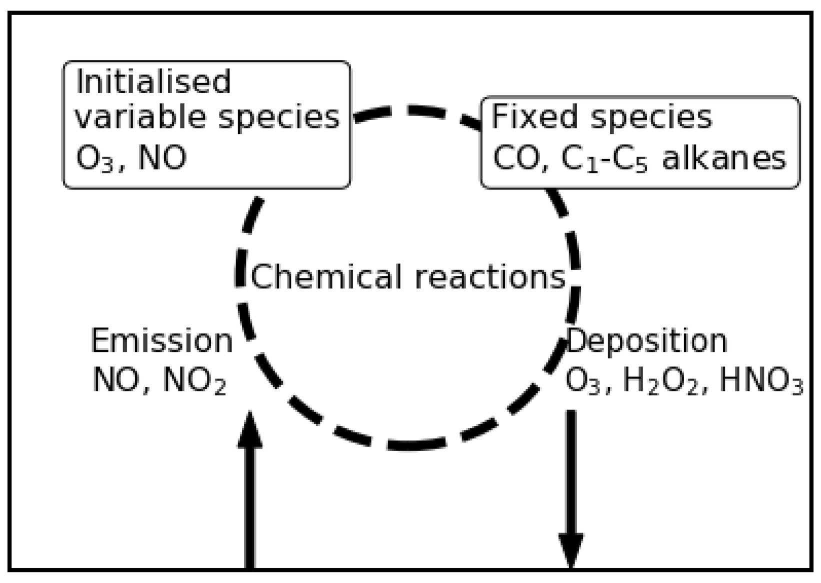
Introduction

Alkyl nitrates ($RONO_2$) are directly emitted or photochemically produced from the oxidation of hydrocarbons in the presence of nitrogen oxide (NO). Their formation terminates the tropospheric ozone (O_3) production by temporarily storing the active form of nitrogen. Due to a relatively long lifetime of a few days to a few months, **$RONO_2$ can be destroyed far away from their sources by photolysis or hydroxyl radical (OH) oxidation, releasing nitrogen dioxide (NO_2) to the local atmosphere and altering O_3 concentrations**.

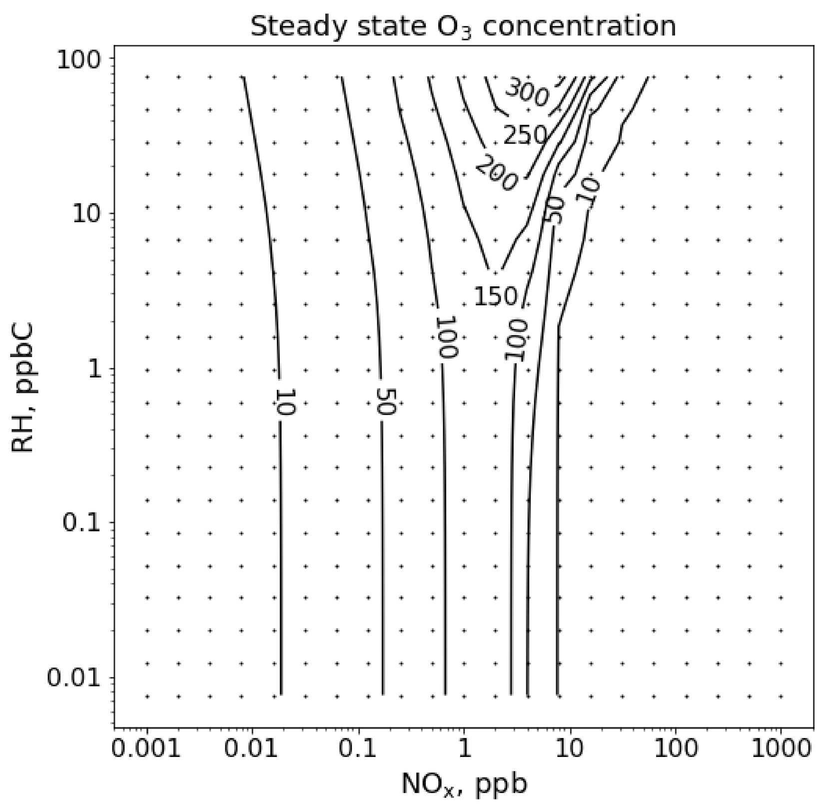


Few studies have investigated the impact of $RONO_2$ chemistry on O_3 using a global chemistry-climate model. Here we **extend the tropospheric chemical mechanism (CheT) of the United Kingdom Chemistry and Aerosols (UKCA) model to include of C_4-C_5 alkanes (RH) and C_2-C_5 $RONO_2$**. We (1) test the new mechanism in a box model using the Master Chemical Mechanism (MCM) as a benchmark, (2) validate the new chemistry against NASA ATom-2 [1], (3) evaluate the impact of C_1-C_5 $RONO_2$ on O_3.

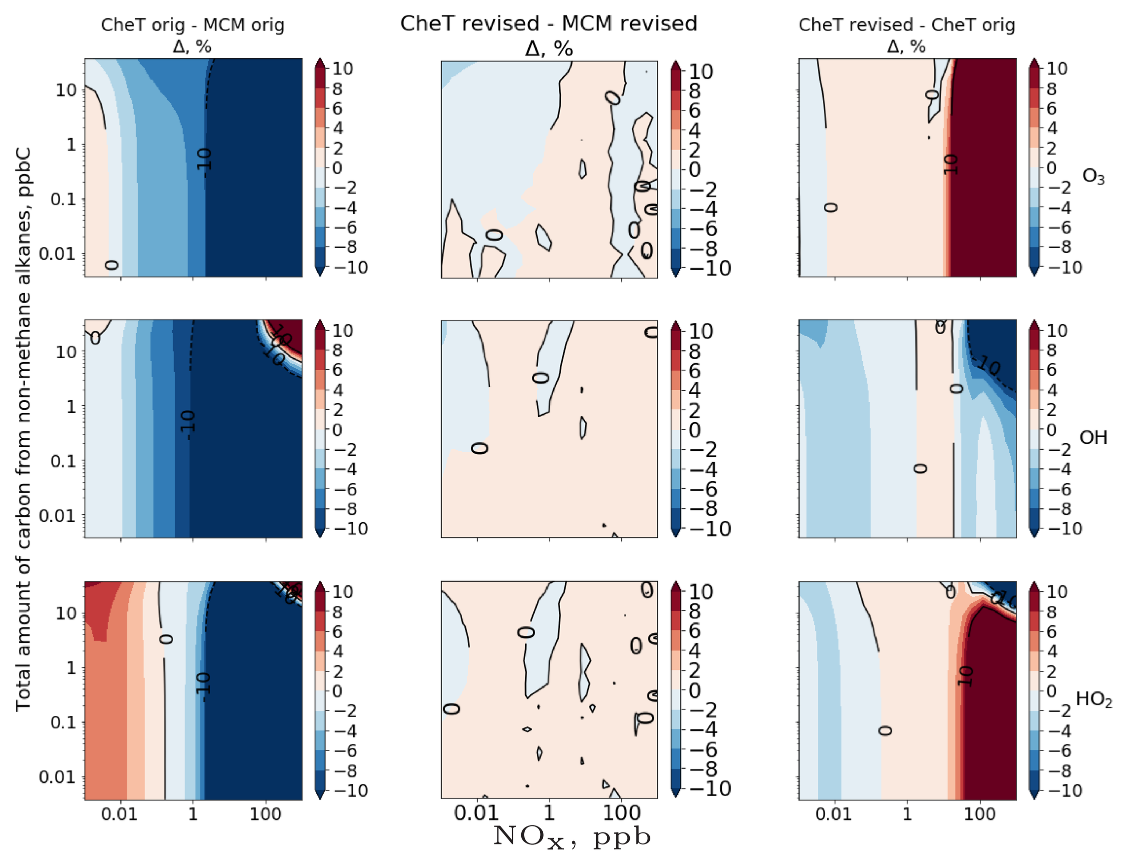
Box model



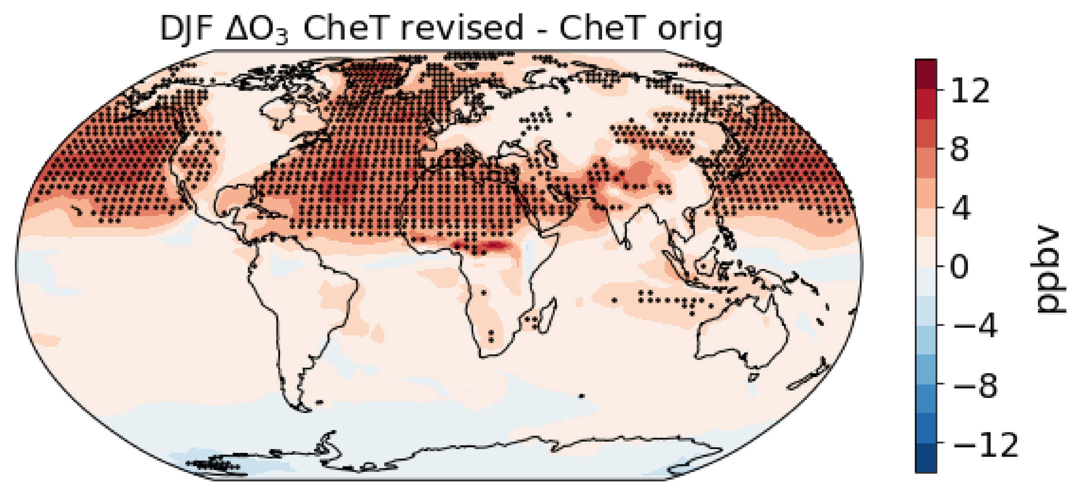
- Chemical mechanisms were compared in a range of NO_x-RH conditions using isopleths plots of 24 hour average concentrations.



Updating chemical kinetics

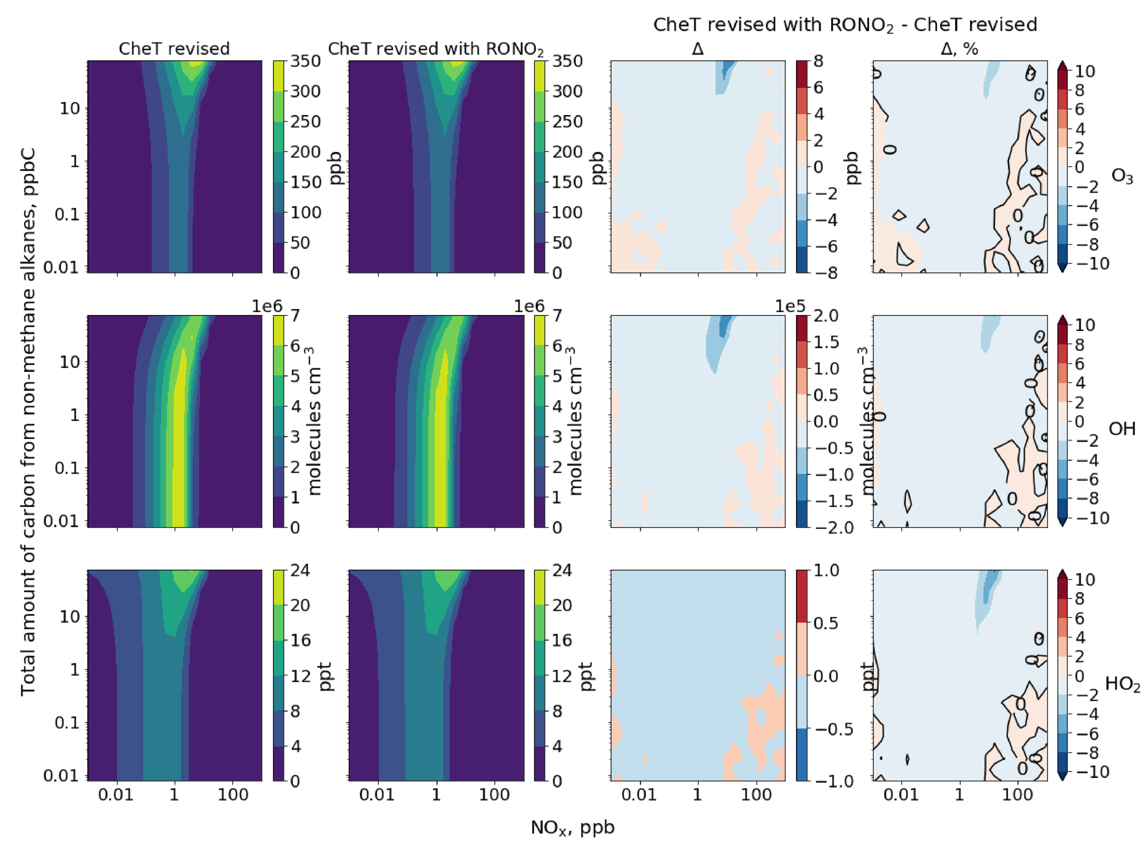


- Updating MCM and CheT inorganic and C_1-C_3 RH chemistry reduces the differences in oxidants between mechanisms in a box model.



- Updating the same chemistry in UKCA reveals statistically significant differences in seasonal mean surface O_3.

Impact of C_1-C_5 $RONO_2$



- C_1-C_5 $RONO_2$ chemistry lowers steady state O_3, OH and HO_2 by 2% in almost all NO_x-RH conditions examined in a box model.

$RONO_2$/RH application

- Photochemical 'clock': system of 2 reactions of compounds whose loss mechanisms are similar but reaction rate coefficients differ:

$$RH + OH \xrightarrow{k_1} RONO_2, \quad RONO_2 + OH \xrightarrow{k_2}$$

- Idea: use $RONO_2$ and RH firn air data from NEEM, Greenland, to better constrain O_3 trends in the NH since 1950 [2].

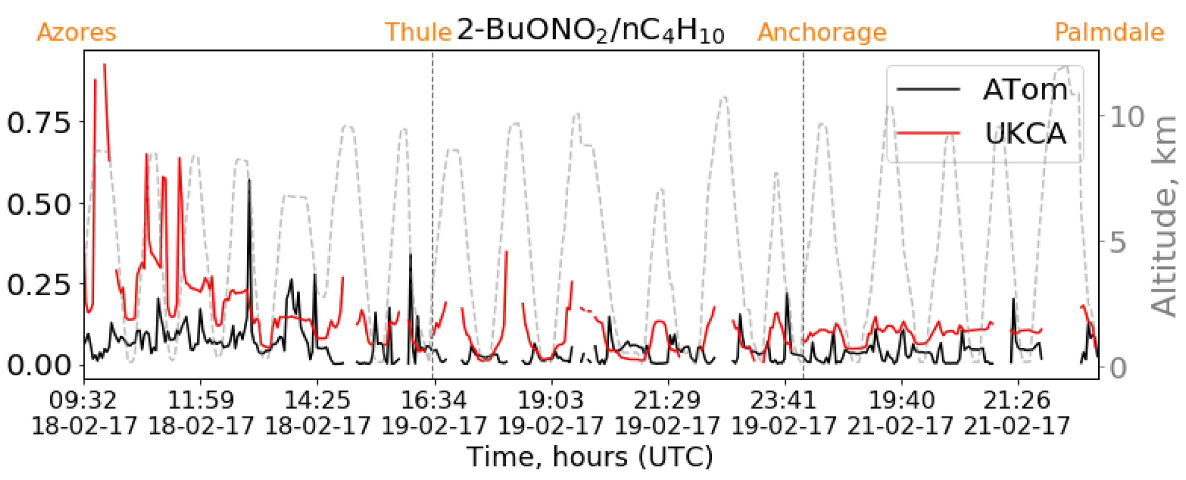
UKCA vs ATom-2

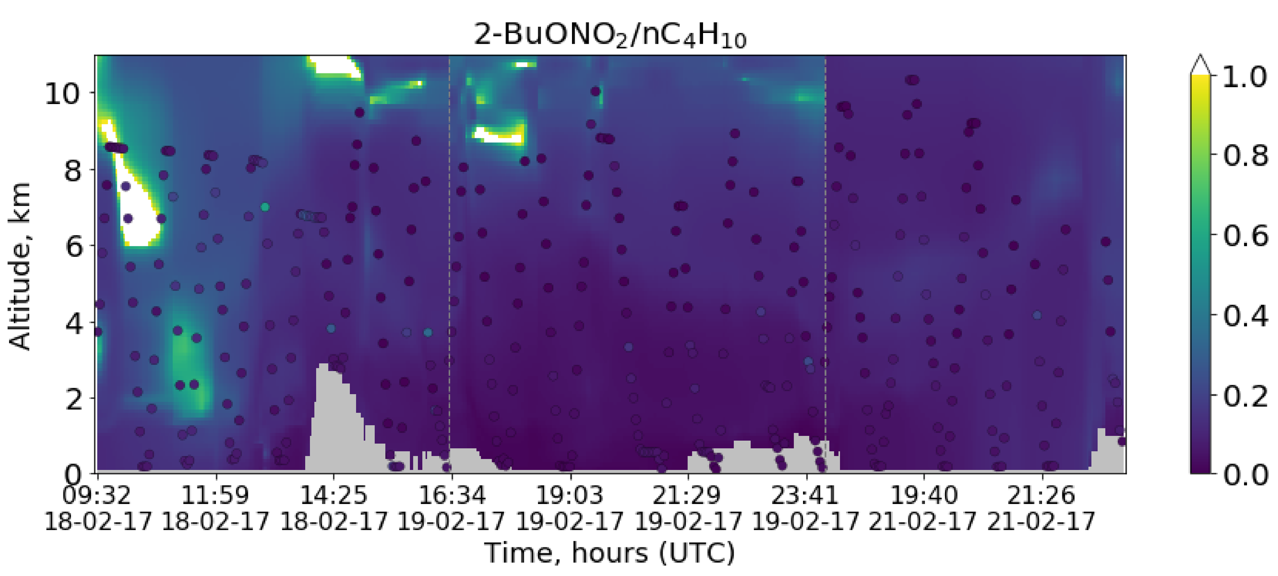
We use NASA ATom-2 [1] Azores-Thule-Anchorage-Palmdale flight data to evaluate UKCA's ability to simulate winter $RONO_2$/RH in the NH.

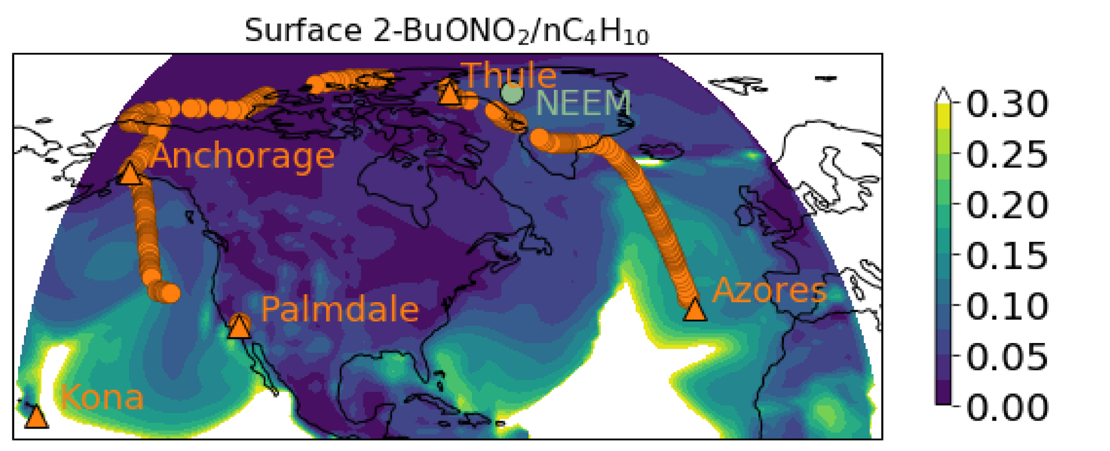
UKCA version	10.6 GA 7.1 N96L85
Meteorology, SSTs	ERA-Interim, Reynolds
Chemistry	CheST+GLOMAP+OXBUDS*
Emissions	RCP 8.5
Initial conditions	OXBUDS* control run

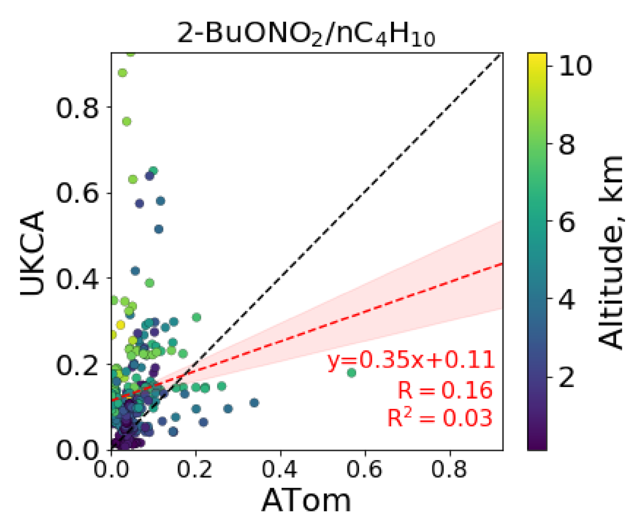
*Please see poster 4.136 by Köhler et al.

- C_4-C_5 RH and $RONO_2$ are underestimated by UKCA, mostly over land and near pollution sources. However, the order of magnitude of C_4-C_5 $RONO_2$/RH is captured reasonably well.









References

[1] Prather et al. Global atmospheric chemistry - Which air matters. *ACP*, 17(14):9081–9102, 2017.
[2] Newland et al. Changes to the chemical state of the Northern Hemisphere atmosphere during the second half of the twentieth century. *ACP*, 17(13):8269–8283, 2017.

Conclusion

- Updating chemical kinetics in UKCA has a statistically significantly impact on O_3.
- UKCA captures winter C_4-C_5 $RONO_2$/RH order of magnitude.
- $RONO_2$ impact on O_3 in a box model is small.

Future work

- Implement interactive C_4-C_5 RH and C_2-C_5 $RONO_2$ chemistry into UKCA.
- Run UKCA with and without $RONO_2$ and evaluate differences in O_3, HO_x and NO_x burdens and distribution.