Institute for Advanced Sustainability Studies (IASS)

The Influence of Atmospheric Conditions on the Production of Ozone during VOC Oxidation

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Background

- Surface temperatures predicted to increase due to climate change.
- What are the effects of increased temperatures on air quality?
  - Increased emissions from vegetation (BVOCs).
  - Increased reaction rates atmospheric chemistry.
  - ...
- What are the effects of increased temperatures on tropospheric ozone concentrations?
  - Increased VOC emissions, especially BVOCs such as isoprene, are well-known to produce large amounts of ozone per molecule of VOC emitted.
  - Increased temperatures means that the PAN sink for peroxy radicals and NO_2 is much less-effective at transporting RO2 and NO_2 away from emission sources due to increased thermal decomposition rates.

  $\Rightarrow$ Future increases in ozone levels.

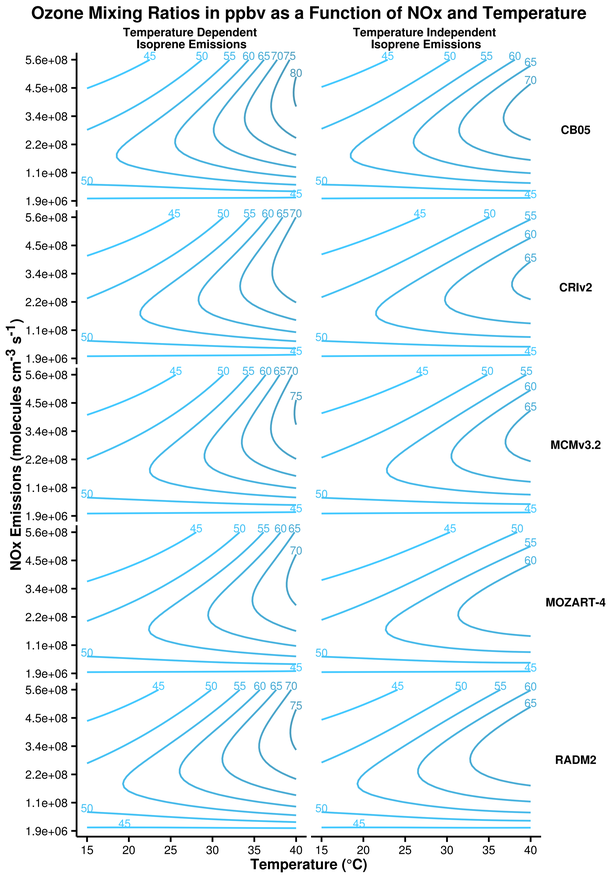
Motivation

- Ozone levels over central europe are known to be driver by temperature. i.e. increases in temperature correlate with increases in ozone.
- Also confirmed in many studies over western and eastern US.
- This correlation is shown in many observational studies but modelling studies have tended to focus on the effects of increasing temperature on ozone under specific atmospheric conditions.
- How would changing NOx emissions influence the ozone produced with increases in BVOC and chemistry?
- Are increased BVOC emissions or increased chemistry more dominant?

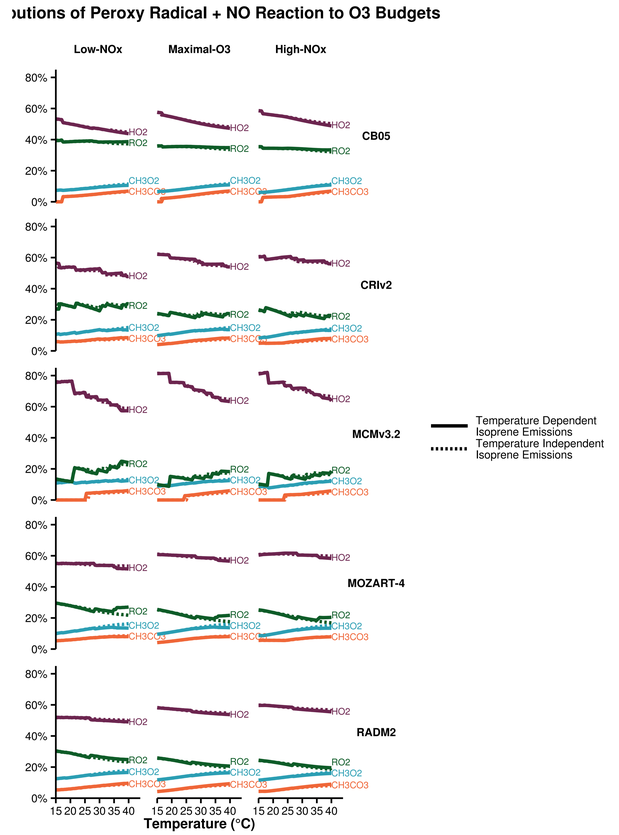
Approach

- Idealised box model simulating central europe (Benelux).
- Systematic variations in NOx over temperature range (15 – 40 °C).
- Simulations repeated using temperature dependent and independent source of isoprene emissions.
- Further repetitions usings chemical mechanisms that represent atmospheric chemistry at different scales: Point - MCMv3.2; regional - CRIv2, RADM2, CB05; global - MOZART-4.

Results



- Non-linear relationship of ozone mixing ratios with NO_x and temperature, reproduced by all chemical mechanisms.
- Higher ozone produced using RADM2 and CB05 compared to detailed chemistry of MCMv3.2.
- Increased ozone when including temperature dependent source of isoprene, especially at high-NO_x.
- Lower NO_x levels have lowest ozone mixing ratios with both temperature dependent and independent source of isoprene.



- Assigned the ozone produced to three NO_x-regimes based on H_2O_2/HNO_3.
- The contributions of the reactions of peroxy radicals with NO to O_x (= $O_3 + NO_2$) production budgets are determined for each NO_x-condition.
- Contributions of methyl peroxy (CH_3O_2) and acyl peroxy (CH_3CO_3) to O_x budget increases with temperature.
- CH_3CO_3 is a precursor of CH_3O_2 which in turn is a precursor of HO_2. Thus increased source of a precursor of CH_3CO_3 - acetaldehyde - leads to higher ozone production.
- Acetaldehyde is an important carbonyl product, especially during isoprene degradation, and in CB05 and RADM2 it as a much higher yield, due to a lack of representation or underestimation of the ketone yield from VOC oxidation.

Conclusions

- Lower NOx levels produces the least amount of ozone regardless of the increases of emissions and chemistry. Thus, target decreases in NO_x emissions.
- All chemical mechanisms reproduce the non-linear relationship of ozone on NO_x and temperature.
- CB05 and RADM2 over-estimate the increases of ozone with temperature compared to detailed chemistry of MCMv3.2.
- The treatment of secondary chemistry in CB05 and RADM2 promotes ozone production through more aldehyde production at the expense of ketones which leads to increased levels of acyl peroxy radical (CH_3CO_3). The further degradation on CH_3CO_3 produces more ozone.

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