

Meteorology and Ozone, Temperature - Outline

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1 Objective

Many observational studies have noted an almost linear increase of ozone levels with temperature. The reasons for this increase are two-fold – temperature-dependent emissions of ozone precursors, the most important being the increase in isoprene emissions from vegetation, and temperature-dependent chemistry leading to ozone production. We look at how the relationship between ozone and temperature is represented in idealised simulations using a box model and repeated using different chemical mechanisms across different NO_x gradients. What is more important for the increase of ozone with temperature? Increased emissions of isoprene or the increase in the rates of chemical reactions? How does this change with NO_x?

2 Introduction

2.1 Currently Accepted General Statement

- Many studies, both observational and modelling, have noted an almost linear increase of ozone levels with temperature.
- Main reasons for this increase are the increased emissions of VOC from vegetation, in particular isoprene, and increased chemistry due to the increase in reaction rates, many of which are temperature dependent.

2.2 Specific Problem(s)

- Climate change is due to cause an increase in temperatures world-wide with the potential for aggravating air pollution with increased amounts of surface ozone.

2.3 Gap

- Although observations and many regional modelling studies have shown a strong dependence of O₃ production and temperature, there has been (to our knowledge) no detailed modelling study looking at the relationship of O₃ on NO_x and T as represented in models. And furthermore in different chemical mechanisms used by models.

2.4 Study Objective/Scientific Question/Hypothesis

- Determine what is more important: emissions or chemistry, for increased ozone with temperature under different NO_x-regimes.
- Compare simulations of different chemical mechanisms and see how they re-produce the observed relationship.

3 Methodology

3.1 Experimental Design

- Box model to focus on the chemical details of what is causing increases of ozone with temperature.
- Simulations with systematic variations in temperature and NO_x for a set of initial AVOC emissions, repeated using a temperature-dependent and temperature-independent source of isoprene.
- Repeat simulations using different chemical mechanisms to see whether the relationship between ozone and temperature is reproduced by different representations of the chemistry.
- Temperature varied from 15–40 °C and NO_x emissions (represented as NO emissions) from

3.2 Model Setup and Simulations

- MECCA box model used in Coates:2015 but updated to include a diurnal mixing layer and exchange with the free troposphere.
- Broadly representing the central european area of Benelux (Belgium, Netherlands, Luxembourg), thus using solar zenith angle of 51 °C where temperature is a driver of ozone production (Noelia:2015).

3.3 Initial Conditions

- See paper draft so far.

4 Results

4.1 Ozone Contours

- Figure plot of contours TD and TI experiment for all mechanisms.
- Non-linear relationship of peak O3 with NOx and Temperature reproduced by each chemical mechanism.
- **Diff from MCMv3.2:** RADM2 and CB05 produce the larger amounts of ozone compared to more detailed MCMv3.2 chemical mechanism, especially at higher NOx levels. The maximum percentage increase from the MCMv3.2 simulations is 8 % for RADM2 and 13 % for CB05 for the TI runs and 7 % and 10 % for RADM2 and CB05 in the TD runs, this maximum occurs under high temperature and high NOx in both experiments (top-right hand corner in contour plots). MOZART-4 produces at most 8 % lower ozone than MCMv3.2 in both the TD and TI runs, again when having high temperatures and high NOx. CRIv2 produces similar amounts of ozone to MCMv3.2 throughout the range of temperatures and NOx.
- **Diff between TD and TI:** When including a temperature-dependent source of isoprene, there is an increase in ozone when using each chemical mechanism, the largest increases from the TI case is at the highest temperature (40 °C) and at higher NOx emissions. In MCMv3.2, CRIv2 and MOZART-4 the largest increase of ozone produced by the increased isoprene emissions is around 30 %, while in RADM2 and CB05 an increase of about 20 %.

- At low NO_x emissions, there is not much increase in ozone even when increasing temperature regardless of chemical mechanism.
- **Increase from reference to maximum Temperature :** Assigning each model run from the NO_x-T matrix of runs to a NO_x-regime (Low-NO_x, Maximal-O₃, High-NO_x) based upon the value of the HNO₃ to H₂O₂ ratio in Sillman:2015, Then calculating the mean O₃ in each of the three NO_x-regimes we determined the increase in ozone due to increased chemistry from the TI runs and then the added increase from the TD source of isoprene by comparing the difference in ozone produced at our reference temperature (20 °C) and the highest temperature in the study (40 °C).
- Results in Table: In each NO_x-regime, CB05 and RADM2 have the largest increase in ozone between temperatures in the TI runs (High: about 37 %, Maximal-O₃: about 28 %, Low: about 18 %), but then when including the TD source of isoprene, the ozone increases an additional 17 % in High, 12 % in Maximal-O₃ and 8 % in Low. Compared to MCMv3.2, CRIv2 and MOZART-4, where the increases in ozone due to chemistry alone are less than those in CB05 and RADM2 but when including a temperature-dependent source of isoprene, the percentage of additional ozone due to increased emissions is higher (especially High and Maximal NO_x regimes) but not much difference in Low-NO_x regime.

4.2 Ox Production Budgets

- Determine budgets of Ox (= O₃, NO₂, NO₃, N₂O₅, RO₂NO₂) to look at the effects of reactions of peroxy radicals with NO that produce NO₂ which goes on to produce O₃.
- All simulations split into a NO_x regime: Low-NO_x, Maximal-O₃ and High-NO_x based on ratio of HNO₃ to H₂O₂ as defined by Sillman:1995. The mean of contributions of each peroxy radical reaction with NO to the total Ox budgets in each NO_x regime is determined.
- HO₂ reaction with NO is always the highest contributor but at higher temperatures its fractional contributions decrease because of the increased contributions of other peroxy radicals.
- The contributions of acyl peroxy radicals, eg. CH₃CO₃, those radicals that go on to produce RO₂NO₂ on reaction with NO₂, show an increase in their contributions with temperature.

- Non-acyl peroxy radicals, e.g. CH_3O_2 , show little change in the contributions to the Ox budget.

- How is this contribution different with different mechanisms?

- Quantitative results

4.3 Comparison to Observed Results

- ERA-Interim gridded data over Europe for the years 1998–2012, has been shown to indicate that in many regions over central Europe, ozone production is driven by temperature(Noelia:2015).
- This data is base on observations from the measurement station network across europe and includes data for the mean 8-hr max O3 as well as the daily maximum temperature.
- We show the observed relationship between ozone and temperature for many sub-regions of central Europe and look at the slopes of this relationship (m_{O_3-T}).
- We compare the simulated m_{O_3-T} for our model runs in eaCh chemical mechanism to these different regions.
- The slope of the O3-T linear regression line is dependent on the NOx conditions and so we also compare the simulated slopes for each NOx-regime as detemined by the H2O2:HNO3, similar to Section Ox Production Budgets.
- Missing results

5 Discussion

5.1 Ozone Contours

- **Increase from MCMv3.2:**
- **Increase with higher isoprene source:** The ozone produced when using a temperature-dependent source of isoprene in RADM2 and CB05 is lower than in the other chemical mechanisms, indicating that it is the treatment of isoprene degradation in RADM2 and CB05 that is causing this slower response to increased emissions.

- Out of the chemical mechanisms used in our study, CB05 and RADM2 describe isoprene degradation with the least amount of species (CB05 - 24, RADM2 - 18) and also use the least amount of species specific to isoprene degradation (CB05 - 2, RADM2 - none). Compared to MOZART-4 which describes isoprene degradation using 33 species, 14 of which are unique to isoprene oxidation.
- Isoprene degradation is known to be a source of ozone due to the large amount of peroxy radicals produced during its degradation and also the importance of the degradation products methacrolein and methyl vinyl ketone. These two major degradation products are not included in either CB05 or RADM2, and the lack of species also means that less peroxy radicals are produced which in conditions with enough NO_x, would further catalyse ozone production.
- **Increase from reference temperature:** Looking at the increases in ozone from the reference temperature of 298K, indicates that while in each case the largest increases are due to increased chemistry rather than increased isoprene emissions as the percentage increase from chemistry alone is higher than that when adding a temperature dependent source of isoprene. Largest increases in High-NO_x.
- The differences in the response between the mechanisms indicates that the chemistry in CB05 and RADM2 is much more temperature-sensitive, especially at higher NO_x levels than in the other chemical mechanism. However, as noted previously, CB05 and RADM2 seem to underpredict the ozone produced from isoprene degradation leading to a lower increase in temperature in these mechanisms.

5.2 Ox Production Budgets

- test

5.3 Comparison to Observed Results

- test

6 Conclusions

- Do chemical mechanisms represent the observed relationship between ozone and temperature? Yes. with NOx gradients similar contours show a non-linear relationship between O3, NOx and Temperature as noted in Pusede:2014. But RADM2 and CB05 predict a higher sensitivity of ozone to temperature due to their representation of NMVOC chemistry; in particular the lack of ketones and rather aldehydes which promote ozone production.
- What is more important for increasing ozone with temperature: isoprene emissions or chemistry? Isoprene emissions, as the increasing isoprene emissions with temperature as predicted by MEGAN2.1 give increases of up to 16 ppbv of ozone, depending on the NOx levels.
- How do the results compare to observed? Comparing the gradient of ozone with temperature at the different NOx-regimes in our simulations to the observed regions over europe (ERA-Interim data)...
- Future temperature scenarios: Climate change is due to cause an increase in global temperatures, thus in locations with high NOx emissions and with vegetation know to emit isoprene, we expect increases in surface ozone. However, dramatically reducing NOx emissions would shift the atmospheric regime to a low-NOx regime would minimise the increases of ozone with temperature. Despite increased isoprene and increased chemistry.