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 NOx 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 NOx?

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 NOx 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 NOx-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 NOx 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 NOx 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 chemcial 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 and7 % 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 NOx 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 NOx-T matrix of runs to a NOx-regime (Low-NOx, Maximal-O3, High-NOx) based upon the value of theHNO_3 to H_2O_2 ratio in Sillman:2015, Then calculating the mean O3 in each of the three NOx-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 NOx-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 NOx regimes) but not much difference in Low-NOx regime.

4.2 Ox Production Budgets

- Figure: Budgets of Ox (= O3, NO2, O) allocated to major categories: RO2NO2 (peroxynitrate) decomposition, reactions of the HO2, acyl (ARO2) and non-acyl (RO2) peroxy radicals with NO, other reactions of organic compounds and inorganic chemistry. The RO2NO2 category include HO2NO2, CH3O3NO3 and PAN species; the ARO2 category includes all acyl peroxy radicals such as CH3CO3 that may form RO2NO2 species when reacting with NO2 and the RO2 category includes non-acyl peroxy radicals such as CH3O2 and C2H5O2.

- All simulations split into a NOx regime: Low-NOx, Maximal-O3 and High-NOx based on ratio of HNO3 to H2O2 as defined by Sillman:1995. The mean of each category contributing to the Ox budgets in each NOx regime is determined at each temperature.

- In all NOx-regimes, RO2NO2 decomposition contributes the most to Ox production, followed by the reactions of NO with the HO2, RO2 and ARO2 peroxy radicals and their chemistry is highly temperature dependent as seen in Fig.. The contributions of other organic species and inorganic chemistry are either very minor, as in the former, or temperature-indepedent (the latter).

- **Increase from 20C:** Looking at the maximum increase in Ox production at 40 °C from the reference temperature of 20 °C, RO2NO2 decomposition shows the largest increase in contribution to Ox budget, almost double that of the HO2. Thus the decrease in lifetime of RO2NO2 means that RO2NO2 is not such an effective sink for peroxy radicals and NO2 and these are re-formed quicker at higher temperatures. The peroxy radicals and NO2 may then produce Ox through other reactions.

- **Difference between mechanisms:** RO2NO2 contribution highest in MCMv3.2 for each NOx-condition and the least RO2NO2 production is from CRIv2 and MOZART-4. Contribution from HO2 and RO2 is higher in all non-MCM mechanisms and may compensate for the lower RO2NO2 production in the non-MCMv3.2 mechanisms,

- **RO2NO2 budgets** Breaking down the RO2NO2 budgets in each mechanism shows that the MCMv3.2 is the only mechanism which includes CH3O2NO2, in all other chemical mechanisms the main contributor to RO2NO2 is HO2NO2 followed by PAN. The contributions of HO2NO2 and PAN are higher in non-MCM mechanisms but not high enough to fully compensate for the missing contribution of CH3O2NO2. Moreover, CB05 and RADM2 have the highest contribtions of PAN than other chemical mechanisms even when having a temperature-independent source of isoprene emissions, accordingly the organic source (CH3CO3) is also higher in CB05 RADM2 which leads to higher ozone production through its further degradation.

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_{O3-T}).

- We compare the simulated m_{O3-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 out 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 know 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 NOx, 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-NOx.

- The differences in the response between the mechanisms indicates that the chemistry in CB05 and RADM2 is much more temperature-sensitive, especially at higher NOx 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.