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 that temperature is an important meteorological driver for ground-level ozone (Noelia:2015). In some areas, increases in temperature can lead to an almost linear increase of ozone (refs).
- Main reasons for this increase are the increased emissions of VOC from vegetation, in particular isoprene, and faster chemistry due to the increase in reaction rates, many of which are temperature dependent. (Pusede:2015)
- Observational studies look at the total effect of ozone with temperature, whereas a model can look at the temperature-dependent processes that influence ozone. In other words,

observational studies look at the total derivative of ozone with temperature while models can look at the partial derivatives of the temperature-dependent processes influencing ozone. (equation)

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. Also by performing highly detailed modelling the effects of faster chemistry and increased emissions can be separately analysed.

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 (range) to (range) molecules (NO) cm^{-2} s^{-1}.

3.2 Model Setup and Simulations

- MECCA box model used in Coates:2015 but updated to include a diurnal mixing layer and vertical mixing with the free troposphere.
- Representing urban conditions, we chose the central european area of Benelux (Belgium, Netherlands, Luxembourg), thus using solar zenith angle of 51 °C.

3.3 Initial Conditions

- See paper draft so far.

4 Results

4.1 Ozone Contours

- Figure plot of contours of peak ozone in ppbv with total NOx emissions and temperature for the TD and TI experiments with each chemical mechanism.
- Non-linear relationship of peak O3 with NOx and Temperature reproduced by each chemical mechanism.
- **Diff between TD and TI:** When including a temperature-dependent source of isoprene emissions, 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.
- Lowest increase in peak ozone is under low-NOx conditions for each chemical mechanism regardless of the source of isoprene emissions.
- Figure of mean of peak O3 at each NOx-condition, determined based on ratio of HNO3 to H2O2 (Sillman:1995). Mean ozone at each temperature in the NOx-regime was used

for plots. Fig. includes indication of where the differences are taken which are reported in table.

- Table of increase in ozone mixing ratios due to chemistry and emissions from the increase in ozone at 40C from reference temperature of 20C. Difference of chemical mechanisms ozone mixing ratios at 40C from MCMv3.2 mixing ratio due to chemistry and emissions also indicated.

- **Increase from reference to maximum Temperature:** Largest increases in ozone at 40C from 20C in high-NOx conditions, the increase in ozone at high-NOx conditions is around double the increase in ozone with low-NOx.

- Largest increase in ozone due to faster chemistry rather than increased isoprene emissions at each NOx-condition and each chemical mechanism.

- **Diff from MCMv3.2:** CRIv2 shows similar increases in ozone due to chemistry and isoprene emissions to the MCMv3.2. MOZART-4 has largest differences due to chemistry at high-NOx conditions from MCMv3.2. CB05 and RADM2 have higher increases in ozone due to chemistry than MCMv3.2, CB05 produces 7 ppbv of ozone more than MCMv3.2 while RADM2 produces 3 ppbv more ozone. Increase in ozone due to increased isoprene emissions in RADM2 is lower 3 ppbv than that of the MCMv3.2.

4.2 Ox Production Budgets

- Figure: Budgets of Ox (= O3, NO2, O) allocated to categories contributing to Ox production: RO2NO2 (peroxynitrate) decomposition, reactions of the HO2, acyl (ARO2) and non-acyl (RO2) peroxy radicals with NO, other reactions of organic compounds and inorganic reactions. The RO2NO2 category includes HO2NO2, CH3O2NO2 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.

- Production budgets are normalised by total loss rate of emitted NMVOC, Fig. (no) displays the number of molecules of Ox produced per molecule of NMVOC oxidised. As the temperature increases, the reaction rates of most of the reactions speeds up, including the rate at which the emitted NMVOC are oxidised. In fact, the dual effects of increasing

isoprene emissions and faster oxidation rates are effectively constant in both cases (a) the temperature-dependent emissions and (b) temperature-independent emissions of isoprene. In the case of the MCMv3.2, 7 molcules of Ox are produced per molecule of NMVOC oxidised, all the reduced chemical mechanisms produce up to 2 molecules of Ox per molecule of NMVOC oxidised less than MCMv3.2.

- Pusede:2015 indicates that the RO2NO2 lifetime decreases with temperature, making it a less effective reservoir for peroxy radicals and NO2. Production of Ox increases with temperature due to faster chemistry which speeds of the degradation of NMVOC, promoting radical production which in the presence of NOx produces Ox. Peroxy radicals can also react with NO2 to form RO2NO2, an important reservoir for peroxy radicals and NOx at low temperatures whereas at high temperatures, thermal decomposition speeds up which quickly re-releases RO2 and NO2, which may lead to more Ox production.

- The increased thermal decomposition of RO2NO2, which makes it a less effective reservoir for acyl peroxy radicals and NO2 increases with temperature. Concurrently the effects of inorganic processes (mainly ...) decreases with temperature.

- 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. The contributions of these categories are highly temperature dependent, with a maximum at 40C and minimum at 15C. The contribution of inorganic chemistry to Ox production is constant with temperature.

- When using a temperature-dependent and temperature-independent source of isoprene emissions, Ox production is maximum at the highest temperature. At 40C, the contribution of RO2NO2 decomposition to Ox production is almost double the contribution of HO2 to the Ox budget in the MCMv3.2. From the reduced chemical mechanisms, CB05 and RADM2 have larger contributions of RO2NO2 to Ox production than 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 these reduced chemical mechanisms,

4.3 Comparison to Observed Results

- ERA-Interim gridded data over Europe for the summers of 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 based 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 the maximum 8-hour mean of ozone and daily maximum temperature for sub-regions of Europe and plot overlay the ozone mixing ratios obtained in each NOx-condition for the temperature-dependent simulations.

- 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.

- The model does not capture the rate of increase of ozone with temperature. The ozone mixing ratios at lower temperature are over-estimated and the ozone mixing ratios at higher temperatures are under-estimated. Thus the chemical mechanisms are less-senstive to temperature as the real-world observations. The WRF-Chem model results, using RADM2 and MOZART-4 chemistry, (does this look more like the observations or the model?)

5 Discussion

5.1 Ozone Contours

- **Increase from MCMv3.2:**

- **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. Need to look at Ox production budgets to analyse and determine which chemical processes are the most important.

- 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. The analysis of the Ox production budgets leads to the answers for this.

5.2 Ox Production Budgets

- Analysis of RO2NO2 budgets indicates that the increased RO2NO2 in the MCMv3.2, that is the main difference in Fig. (no) is die to the inclusion of CH3O2NO2 reservoir in the MCMv3.2. No reduced chemical mechanism used in this study includes CH3O2NO2 chemistry. In fact, the RO2NO2 per molecule of NMVOC oxidised of all other RO2NO2 is very similar between all chemical mechanisms. Thus, including CH3O2NO2 chemistry would aid in capturing the Ox production described by the MCMv3.2.

- 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.

- Further analysis of the RO2NO2 budgets in each mechanism shows that the MCMv3.2 is the only mechanism which includes CH3O2NO2 production. CH3O2NO2 is the peroxynitrate formed from the methyl peroxy radical, CH3O2, and NO2.

Literature on its importance?

- 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 contributions 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 and RADM2.

- The main source of CH3CO3 is acetaldehyde (CH3CHO) which is a common secondary degradation product of many emitted NMVOC, as well as being emitted into the troposphere. In Coates:2015, RADM2 was noted to underestimate the production of ketones from the emitted species HC3 (representing many less-reactive NMVOC including alkanes, alcohols, alkynes). Thus the main carbonyl produced is acetaldehyde which promotes PAN and in turn ozone production through the secondary degradation of CH3CO3. Moreover, CB05 does not represent any ketone species while the secondary degradation of many species produces CH3CHO with the same result of higher PAN and ozone production.

5.3 Comparison to Observed Results

- Observations include other temperature-dependent process that are not included in our simulations, the most important of which is that our simulations do not include stagnation.
- Also, we have concentrated our study on the increase of isoprene emissions with temperature, in reality many other NMVOC are emitted from vegetation with increased temperature (Guenther:2006).

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.
- Chemical mechanisms can represent the non-linear chemistry of ozone with temperature and NOx but this chemistry is not as senstive as observational results.

- Most of these increase (result) is due to faster chemistry and not increased isoprene emissions with temprature. Out of the faster chemistry, it is the decrease in the lifetime of RO2NO2 species that has the largest influence on ozone mixing ratios.

- In all experiments, conditions with high-NOx leads to more ozone with temperature. At low-NOx conditions, the increase of ozone with temperature is minimised and thus reducing NOx emissions could minimise the effects of increasing ozone with temperature.