

Meteorology and Ozone, Temperature - Outline

J. Coates¹ and T. Butler¹

¹Institute for Advanced Sustainability Studies, Potsdam, Germany

December 14, 2015

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 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 NO_x 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 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 (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 NO_x emissions and temperature for the TD and TI experiments with each chemical mechanism.
- Non-linear relationship of peak O₃ with NO_x 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 NO_x emissions.
- Lowest increase in peak ozone is under low-NO_x conditions for each chemical mechanism regardless of the source of isoprene emissions.
- Figure of mean of peak O₃ at each NO_x-condition, determined based on ratio of HNO₃ to H₂O₂ (Sillman:1995). Mean ozone at each temperature in the NO_x-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 molecules 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 NO_x produces Ox. Peroxy radicals can also react with NO₂ to form RO₂NO₂, an important reservoir for peroxy radicals and NO_x 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 the excited oxygen atom O(1D) deactivated to a ground-state oxygen atom O) decreases with temperature.
- 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 each category contributing to the Ox budgets in each NO_x regime is determined at each temperature.
- In all NO_x-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 NO_x-condition for the temperature-dependent simulations.
- The slope of the O₃-T linear regression line is dependent on the NO_x conditions and so we also compare the simulated slopes for each NO_x-regime as determined 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-sensitive 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-NO_x. 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 NO_x 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 due 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 peroxyxynitrate formed from the methyl peroxy radical, CH₃O₂, and NO₂.
- 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

Literature
on its
importance?

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 NO_x gradients similar contours show a non-linear relationship between O₃, NO_x 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 NO_x levels.
- How do the results compare to observed? Comparing the gradient of ozone with temperature at the different NO_x-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 NO_x emissions and with vegetation know to emit isoprene, we expect increases in surface ozone. However, dramatically reducing NO_x emissions would shift the atmospheric regime to a low-NO_x 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 NO_x but this chemistry is not as sensitive as observational results.
- Most of these increase (result) is due to faster chemistry and not increased isoprene emissions with temperature. 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-NO_x leads to more ozone with temperature. At low-NO_x conditions, the increase of ozone with temperature is minimised and thus reducing NO_x emissions could minimise the effects of increasing ozone with temperature.