

This paper discusses decadal trends in ozone and ozone precursors in London using routine monitoring observations and a chemical model. The topic is interesting. However, at present the analysis is insufficient and the text lacks focus. The following major issues need to be addressed before the paper can be considered for publication.

Introduction

Paragraph 1 describes what is known about ozone trends in Europe. The summary needs additional clarity and is in places contradictory. If I understand correctly peak O_3 is decreasing but 8 h average and background O_3 are increasing. It would be useful to directly address why the different metrics have responded to precursor changes differently. The authors need a clearer account of previously reported trends and to provide a brief synthesis of the observations in a way that motivates their own analysis.

Paragraph 2 needs to be more thorough. The provided description of the ozone chemistry is insufficient. Because the analysis aims to separate local O_3 chemistry from transport/background effects on observed O_3 abundances, a basic description of the nonlinear dependence of O_3 production on its precursor species is warranted. Briefly describe the nonlinear dependence of O_3 chemical production (PO_3) on emissions. Discuss chemical loss of O_3 to titration at high NO as a distinct process. State how these terms as well as transport and deposition impact measured O_3 concentrations. A discussion of the nonlinear PO_3 and O_3 titration in the context of what O_3 averaging (i.e. peak, daily mean, 8h) is under consideration would be useful to this analysis.

Observations

Measured VOCs include “26 non-oxygenated non-methane C_2 - C_8 hydrocarbons”. This is a very narrow subset of the total VOC mix from both a source and an OH-reactivity perspective. From statements later in the text I infer that none of the VOCs are biogenic in origin. I am not convinced that scaling up the inventory using these observations gives an accurate estimate of the total VOC. Different categories of emissions will be captured by the inventory to varying extent. If unfunctionalized hydrocarbon emissions are among the best constrained by the inventory then the estimate for the total could still be an under prediction. Secondly, explanation is needed as to how VOC at the near-roadway site give an accurate description of the total OH reactivity in suburban and rural locations. I’d guess that the urban wintertime VOC is reasonably well represented, but the summertime total VOC is too low. The uncertainty in the total VOC needs expanded discussion.

If R_{OH} is the concentration of a given species weighted by its reaction rate with OH, then what does this sentence mean: “The same procedure was used for the reactivity calculations, except that total photochemical ozone creation potential (POCP) weighted NAEI emission were used to account for difference in reactivity.”? Is R_{OH} of the total VOC not then how it is defined it on page 1292 line 25? A definition of POCP is needed.

Why have VOCs not been deseasonalized while NO_x has? Neither the motivation nor impacts of this decision are clear to me. Please explain. Also, what does deseasonalizing the data entail?

What methodology is used to measure NO_2 ? Is the technique selective for NO_2 ? If not then the measured NO_2 will be subject to positive interferences from higher oxides of nitrogen. Decreases in NO_x emissions like the authors describe will also impact the abundance of organic nitrates and nitric acid, where these impacts will also be a nonlinear function of NO_x . Could this influence the observed trends, i.e. cause the slower rates of decrease in NO_2 compared to NO ?

Page 1296, line 5: A reduction in congestion would decrease NO_x emissions. This could happen on a fast timeline like the authors describe but would not change $\text{NO}:\text{NO}_2$ unless accompanied by an adequately large change in O_3 or higher nitrogen oxide production. Emission controls affecting emission factors are not implemented this quickly. New vehicle technologies require fleet turnover and this takes time. I need more evidence to be convinced by this argument especially because the other near-roadway sites do not observe the same flattening of the trend (Table 1).

Page 1296, line 28: This problem sounds surmountable.

Modeling

There is insufficient information/discussion provided on the VOC emissions in the model. If the total VOC is too low, the conclusions will be to predict PO_3 that is incorrectly NO_x suppressed.

Please explain the reasoning behind each of the four modeling experiments. What information are you targeting with these tests?

Site selection

I understand that the 5 London sites were selected because they had sufficient data coverage. That said, what insights about chemistry and/or transport are offered by the locations of these sites? Please explain. For example, have these sites been selected because they are located in what you expect to be difference NO_x/VOC PO_3 chemical regimes? Does each site allow a unique test of your model?

It's not clear to me how the site that is the least well predicted by your model is the site from which the NO_x speciation and VOC are derived.

Analysis of observations

Page 1298, lines 1–13: The authors need to provide a quantitative account of O_3 trends in these different locations and quantitatively attribute these trends to changes in precursor emissions. They should also discuss their contribution as separate from work of others.

Sect. 3.2: Considering the title of the manuscript, this section does not provide sufficient analysis.

Page 1297, lines 15–19: I do not see how the decadal trend in ratio of NO_2 to an estimated bottom-up account of the total VOC reactivity to OH demonstrates the changing oxidative capacity of the London atmosphere. I agree that it suggests that the oxidative environment is changing but it does not offer evidence for that change.

Page 1297, line 19: Each factor affecting PO_3 needs to be discussed. If a term cannot be constrained then the resulting uncertainty needs to be discussed.

Page 1297, line 24: What is the ozone formation potential? How is/is it different from VOC reactivity to OH and POCP?

Page 1297, line 28: The authors have not convinced me that trends observed at the near-roadway site can be extrapolated to other locations within the London urban plume. The data are not comprehensive enough at the other sites to be compelling and the authors have not yet built a reasoned argument strong enough to be convincing.

Sect. 3.3

Page 1298, line 11: The authors state that NO_2 is decreasing as expected between 98 and 08 emissions but spend considerable time in Sect 3.1 explaining why increasing NO_2 is observed.

The authors show that O_3 increases near roadways and at the urban core between a model with 98 emissions and one with 08 emissions. Does the model using 98 emissions reproduce the 1998 O_3 time series?

Fig. 5: The information contained in the 4 panels is not clear to me. The authors show the modeled O_3 across England. Why not just the London plume as the title suggests? The other 3 panels show the difference between the 08 emissions scenario and the 3 other scenarios. Unless I have misunderstood, the authors have not yet shown that the model adequately describes O_3 across England. Fig. 5 bottom right suggests to me an insufficient description of VOC emissions in the model, as controls on anthropogenic VOCs appear to have had the same impact on O_3 in the London city center as they do across the rest of domain.

Sect. 3.4

Paragraph 1: The authors assign the O_3 change not captured by the model to changes in the O_3 of non-local origin. Uncertainty analysis of the modeled O_3 is needed here.

Looking at the network of monitors pictured in Fig. 1, concluding that non-local effects are important should be easily verified with measurements. Observational evidence is needed.

Page 1300, line 12: The authors state that although there were “significant reductions” in NMVOC over the study period the VOC speciation did not change. The references cited discuss light-duty vehicle VOC emissions only. It makes sense that these VOCs would be similarly reduced and the speciation of VOCs within this class of compounds would not change. However, what about VOCs of biogenic origin? These biogenic emissions are often highly reactive with OH and are present in large abundances in the summertime. It does not make sense that these VOCs would have decreased at the same rate as the vehicle emissions, thus a substantial change in the VOC speciation is expected.

Page 1300, line 29: The authors need to separate NO_x -suppressed PO_3 from chemical loss to titration by NO both quantitatively and in their discussion of the NO_x emissions effects.

Page 1301, lines 1: Rather than mentioning the observation of a weekend effect in O_3 in other cities, why not present day-of-week observations from the London dataset? This would be one way to check the model’s ability to reproduce O_3 in London.

Page 1301, lines 22–29 and page 1302, lines 1–16: I do not see how this information applies to the analysis performed.