Atmos. Chem. Phys. Discuss., 14, C4830–C4855, 2014
www.atmos-chem-phys-discuss.net/14/C4830/2014/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "The changing oxidizing environment in London – trends in ozone precursors and their contribution to ozone production" *by* E. von Schneidemesser et al.

E. von Schneidemesser et al.

evonsch@gmail.com

Received and published: 14 July 2014

Review of "The changing oxidizing environment in London – trends in ozone precursors and their contribution to ozone production" by von Schneidemesser et al. MS Number: acp-2013-926

Summary:

This paper discusses how ambient ozone concentrations and the photochemical environment of London and the surrounding region have changed in response to changing emissions of ozone precursors. The authors conclude that "roughly half (5 μg

m-3) of the observed increase in urban (London) ozone (10 μg m-3) in the UK from 1998 to 2008 is owing to factors of local origin, in particular, the change in NO:NO2 ratio, NMVOC:NOx balance, NMVOC speciation, and emission reductions (including NOx titration). In areas with previously higher large concentrations of nitrogen oxides, ozone that was previously suppressed by high concentrations of NO has now been "unmasked", as in London and other urban areas of the UK. The remaining half (approximately 5 μg m-3) of the observed ozone increase is attributed to non-local factors such as long-term transport of ozone, changes in background ozone, and meteorological variability.

This analysis presented in this paper may be worthy of publication, but it is poorly reasoned, poorly organized, poorly presented and not quantitatively solid. I recommend that this manuscript be rejected, with encouragement to the authors to completely revise the manuscript essentially from the ground up, paying close attention to the Major and Minor issues detailed below.

Response: Though we may not agree with the main thrust of the reviewer's dismissal, we take the reviewer's comments seriously about overhauling the paper and have considered these points and the individual points below and have made major changes that have significantly improved the paper.

(Note: About one year ago I reviewed essentially this same manuscript for another journal. After completing the present comments below, I reviewed that previous one. It is clear that I raised many of the same issues that I raise again here. Very little improvement has been made to the manuscript since that previous submission. That earlier review is attached at the end of this review in case it is helpful to the authors.)

Response: As outlined in the note to the editor before embarking upon the re-working of the manuscript, we noted that this paper was indeed submitted to another journal previously in another form. However, the previous version of the paper was submitted to Nature. Given the very strict space requirements, I acknowledge that we were not

able to sufficiently address the various aspects of the paper for it to be of the required caliber. In addition, although the reviewer claims that we did not change much between that version and this one, we did address a number of his/her comments in the revisions before submission to ACPD, although clearly not enough. We have taken all of the comments into thorough consideration this time and have hopefully also done so in a manner that addresses them sufficiently.

Major issues:

1) p. 1291, line 9 states that "Data distributions were assessed and determined to be log-normal using q-q plots." This seems reasonable for distributions of primary pollutants, but not for ozone. Please include such plots, at least in the Supplementary Material, and present a clear, robust statistical justification for using a log-normal distribution for ozone. If this is not possible, then please carefully review the analysis to see how the results differ if ozone is actually better described as a normal distribution.

Response: As the reviewer requested, Q-Q plots have been added to the SI (Figure S1) for ozone, CO, and a few NMVOCs to demonstrate that the data are log-normal. Text has also been added to the manuscript to indicate this addition. The plots indicate that the distribution is better represented as log-normal than as a normal distribution.

2) p. 1291, line 16 states that "...; all trends, except those of VOCs, were deseasonalized". Please clearly explain what is meant by "deseasonalized", describe the process involved, discuss why this was deemed necessary, and discuss the how this process affected the results.

Response: Text (including references to the method and previous trend analysis work) was added to explain the process and reasons for deseasonalization. Text added: '. . .were deseasonalized using an stl-based method (decomposition of a time series into seasonal, trend, and irregular components by loess (Wilson et al., 2012;Carslaw and Ropkins, 2012;Cleveland et al., 1990)). For species, such as ozone, which have strong seasonal cycles, removing this seasonality allows for a better assessment of

the underlying trend, e.g., as in (Colette et al., 2011). Although there is likely some seasonal influence on some of the NMVOC species, many do not have a distinct seasonality, and were therefore not deseasonalized, which is consistent with previous trend analysis of NMVOCs (von Schneidemesser et al., 2010).'

3) The trend analysis reported in Table 1 should also be performed for NOX = NO + NO2. This is because measured concentrations of both NO and NO2 are affected by changing total emissions, changing NO2 to NO emission ratios, and changing ambient O3 concentrations, while the sum is affected only by changing total emissions.

Response: The reviewer makes a good point. The NOx trends have been added to Table 1 and integrated into the results and discussion.

4) The trend analysis reported in Table 1 should also be performed for the separate seasons. There may be different emission trends between seasons. This is particularly important for O3, since decreasing titration by NOX may be more important in winter compared to summer.

Response: Seasonal trend analysis has been added to the manuscript. A table (now Table 2) including all of the seasonal data that parallels Table 1 has been added. Furthermore, a figure (now Figure 3) has been added that depicts in detail the seasonal trends by site type for all sites within London. Explicit discussion of these results was added in section 3.1.1. Unfortunately, many of the seasonal trends were not statistically significant and therefore did not allow for as many concrete conclusions as might otherwise be possible.

5) p. 1291, line 24 - CO is omitted from the OH reactivity calculation. How large is the fraction of total OH reactivity that is then not considered? This can be evaluated for the Marylebone Road station where CO was measured.

Response: An evaluation of the contribution of CO to the OH reactivity was added to the manuscript. It was calculated for Marylebone Road, and using the Bexley site (a

suburban site in London with similar time series of NO2, NO, and O3 to the Eltham site), the contribution of CO to the OH reactivity at Eltham was also estimated. The methods section was updated to reflect this and a more detailed discussion was added to section 3.2, including comparison to previous studies and information on OH reactivity measurements from London.

6) p. 1293, lines 6-7 state "the NOx speciation (NO and NO2) is also derived from observations at Marylebone road". Does this mean that the NO2 to NO emission ratio was set equal to the observed ambient concentration ratio of NO2 to NO? Surely, this cannot be correct, since the emitted NOX will come into photostationary equilibrium with the sunlight and O3 on the time scale of a minute or two. Thus, the emission ratio is not directly reflected in the ambient measurements. This requires a clear and complete discussion.

Response: We recognize that simply setting the NO2:NO ratio equal to observed ambient concentrations may not be representative of real life emissions, this was intended as representative of the emissions for the 5x5 grid in the model. However, we aim to conduct a sensitivity study to elucidate the effects of changes, as those observed in the NO2:NO ratios. We use the Marylebone Road data, assuming that these represent 'fresh' emissions, and conditions that are sufficient for such a sensitivity analysis. Furthermore, Carslaw, et al., (2006) [ES&T 40, 6912] reported that 'It is known that these filters [DPF] lead to much higher NO2/NOx ratios than diesel vehicles not fitted with these devices. Typical diesel vehicle NO2/NOx emission ratios without CDPF are 10-15% by volume (17). Reported NO2/NOx ratios (by volume) are in the range of 30-50% (18-20).' These values are very much in the range that we derived from Marylebone Road data. A detailed explanation has been added to the manuscript, including a number of references to justify/explain this. "Moreover, the NOx speciation (NO and NO2) is also derived from observations at Marylebone road: NO2/NOx was 33% and 48% for 1998 and 2008, respectively. These values are derived from measurements, working under the assumption that these are 'fresh' emissions and roughly representative of

tailpipe emissions, given the sampling location directly at the kerbside. In comparison to literature values for NO2/NOx ratios, these values are on the high end for the percent primary NO2, but solidly within reported values (Carslaw, et al., 2006, Ayala, et al., 2002, Tang, et al., 2004, Shorter et al., 2005, Latham et al., 2001). Considering that diesel buses in London were retrofitted with diesel particulate filters which have been shown to significantly increase primary NO2 emissions (Carslaw et al., 2006), these values are not unreasonable for a sensitivity study as we are conducting."

7) p. 1296, lines 2-12 discuss two different trends of NO2 emissions over two different periods. Such analysis is dangerous when dealing with data sets with significant interannual variability, since it is often easy to subjectively select separate periods that have different trends. This discussion is not central to the paper, so I suggest that it be removed. If it is deemed important enough to be retained, then it should be illustrated with a clear figure and a rigorous statistical analysis that clearly demonstrates a high degree of statistical significance for the difference in the trends. This is particularly important, as the remainder of the paragraph discusses that some sites show similar trends, while others do not.

Response: While we find this point of interest, we agree with the reviewer that it is not at all central to the paper, and that the analysis of trends over such short time periods are generally not advisable and have therefore removed it, as well as some of the surrounding discussion.

8) p. 1297, lines 1-13 - It is very important that the seasonal dependence of the O3 trends be clearly discussed - see point 4) above.

Response: We acknowledge that the reviewer makes a good point that a seasonal trend analysis was lacking from the manuscript. We have completed a detailed analysis of seasonal trends, which is now included in the manuscript through an additional Table (now Table 2) and Figure 3. Furthermore, a section discussing the results from this analysis was added to the manuscript in section 3.1.1.

9) Section 3.2 - This section concludes that the ratio of the reactivity of OH with NO2 and with NMVOC has changed dramatically, but this conclusion is based on data from a single site. Data from two other sites are shown for time periods too short to define a significant trend. Therefore the statement "... which seems to indicate that this evolution might not be limited to only roadside locations" is really not justified. It would be better worded as "... which indicates that the reactivity ratio determined at this one roadside location may be more widely representative of European urban areas."

Response: The reviewer makes a good point, and indicates that we were not clear enough with our wording, since we did not intend to indicate that other sites had 'evolved' in the same way, only that other measurements showed that the situation could be more widely representative of other urban areas, as the suggested edit communicates. We have revised the text as suggested.

10) p. 1298, lines 9-11 - The statement "For precursor emissions, the change from the 1998 base case to the 2008 base case model runs showed reductions in NO, NO2, and NMVOCs, as expected (not shown)" is not clear to me. What is "expected"? It would be very useful to compare the model trends for NO and NO2 (and NOX if my suggestion in 3) above is followed) to the measured trends reported in Table 1. This should indeed be shown.

Response: The change in emissions for the base case conditions are now shown in Figure 7 for NOx and NMVOCs. The text has been clarified, since the 'as expected' only referred to the expectation to see reductions in the emissions, in agreement with the measurements, which was not communicated properly. Unfortunately, we cannot compare trends, since we did not model the intervening years, but only 1998 and 2008.

11) With regard to point 4) above, Figure 4 would be much more informative if it were a 4 panel figure showing 3 month averages for the 4 seasons, or even a 2 panel figure showing 3 month averages for the summer and winter.

Response: Figure 4 has been updated to show July and December. The high reso-

lution modelling was only done for selected months, and as we were mainly focusing on the summer period, we are not able to include DJF, which goes into the following year. We feel that July and December are representative of summer and winter time. In addition, the plots were all redone, using the same averaging as for the discussion of the results and the data presented in the table, which are monthly averages of daily max of 8-hour running means, and show the contrast between the seasons. Another option, if it were considered to be much more informative, would be to show 6 panels in the plot of June, July, August and October, November, December. We have this plot, but chose the July, December plot.

12) Attempting to understand Figure 5 is difficult. First, a clearer explanation is required for the 4 different model runs; the terse explanations in Section 2.2 are not adequate. It would be good to guide the reader with clearer explanations as to why each of these emission scenarios was considered. I thought that the left panel in Fig. 4 should be the same as the upper right panel of Fig. 5, but there are differences in color patterns. What is going on here?

Response: The explanation of the model runs has been expanded to include greater details, explaining what the conditions were for each run and what was changed from one to the next. A sentence on the purpose, to elucidate why each run was conducted has also been added to each run description. The reviewer is correct that the left panel in Figure 4 should be the same as the upper right panel of Figure 5. The differences are owing to a slightly different color scale gradient. This has been adjusted so that the scales are identical. The averaging time, as with Figure 4, has been updated for consistency across the entire manuscript. This should hopefully remove any confusion as the plots are now also identical. (Figure 4 is now Figure 8, and Figure 5 is now Figure 9.)

13) p. 1298, line 27 ff - This discussion of the results of the model runs is not clear. The general features should be clearly and concisely discussed here, even if they are discussed in more detail later.

Response: The reviewer makes a good point. The discussion of the model results has been expanded significantly in this section. This should also help to address some of the other comments, and clarify what each of the model runs shows.

14) p. 1299, line 4 ff - The authors discuss "mean daily max 8 h ozone." Is this the same or different quantity as "averaged maximum ozone (all hours)" discussed in the captions of Figs. 4 and 5. It is not clear to me exactly what quantity is being analyzed, plotted – and discussed. This must be crystal clear in any paper accepted for publication. Also I assume that summer in this context is June, July and August, but this should be clearly stated in the paper.

Response: The averaging method for the plots and the text/tables has been made consistent. The average over the specified time period (typically one month or a season) of daily max 8-hour running means, which corresponds to the policy definition, has been used. Furthermore, an explicit definition of the seasons has been added to Sec 2.1, where text on seasonal trends was also included. “The seasons were defined as spring (March, April, May (MAM)), summer (June, July, August (JJA)), fall (September, October, November (SON)), and winter (December, January, February (DJF)), where the winter months are consecutive months (e.g., Dec 1997, Jan & Feb 1998).”

15) Section 3.4 is really the main part of the analysis, but it is very difficult to understand. The writing is not well organized and lacks clarity; it is repetitive in some places. The authors must completely re-evaluate what they intend to say, and then say it with clear, concise descriptions and with improved figures and tables.

Response: We have re-evaluated section 3.4. We have included sub-sections to break up the discussion and have added significant detail on the discussion of the model and observational results. Furthermore we have removed some of the discussion that was not as relevant and refocused this in an additional section – section 3.5 – to discuss factors influencing ozone that were beyond the investigations of the modelling part of our study. Figures have been added, and the existing figures and tables updated and

improved.

16) In the first paragraph of Section 3.4 the authors note that their models can reproduce about 1/2 of the ozone increase observed in London between 1998 and 2008. From this they conclude that 1/2 of the observed ozone increase is due to local conditions, and the other half due to other factors. However, they do not discuss the uncertainty on this result. Given that the models only poorly reproduce ozone observed in London (see Fig. 2) I would not be surprised if the factor of 1/2 is actually a factor somewhere between 0 and 1, a finding that is totally useless. For the authors' conclusion to be valuable, a rigorous discussion of uncertainty is required.

Response: We acknowledge and agree with the reviewer’s point that without a discussion of uncertainty the findings are too general and could mean anything or nothing. That said, a full sensitivity study with many more model runs than would be possible within the scope of this work, is not possible. However, we take the point seriously and have included a more thorough discussion of the model’s validation for reproducing ozone in Europe and the UK, as well as the uncertainty associated with it. Furthermore, we include a much more explicit discussion in section 3.4 with regard to the model results, their uncertainty, and the range within which these results should be placed, to come to a more scientifically robust conclusion.

17) p 1300, line 28 ff - This sentence seems to make no sense.

Response: This sentence has been re-worked to clarify the meaning.

18) p 1301, lines 2-13 - This discussion of the weekday-weekend differences is not clear. The data should be shown in informative figures, and the discussion expanded and clarified. Such a discussion may help to provide the needed uncertainty discussion (see point 16) above).

Response: A much expanded analysis of weekday-weekend differences has been done and also included in the manuscript, including a figure detailing weekday-

weekend patterns for 4 sites within London. A section specifically devoted to discussing these results was also added, now section 3.4.1.

19) The last three paragraphs of Section 3.4 seem to be largely unrelated to the preceding discussion. The authors should develop a clear plan of what they wish to present in this section, and then present that material clearly and concisely in an organized manner.

Response: The reviewer brings up a valid point that the discussion was disconnected from the rest of the manuscript. The discussion around the results and specifically these last 2 paragraphs has been significantly reworked, to include a more thorough analysis of previous trend analysis and factors influencing ozone that were not the subject of our model run study, and more relevant to regional/hemispheric ozone.

20) In the first paragraph of Section 3.4 the authors state "... the remaining 5 μgm$-$3 change in ozone not accounted for by the model, but showing up in the observations can be attributed to non-local influence and other factors, such as changes in (long-range) transport of ozone, changes to background ozone, the influence of biogenic ozone, and the influence of meteorology and natural variability." These factors are not discussed further, but such discussion would likely be productive. In particular, Figures 4-6 seem to indicate that outside urban areas, O3 has generally decreased throughout the model domain. If the above non-local factors were important, would not the non-local influences lead to increases outside of urban areas instead of the calculated decreases?

Response: Figures 4-6 have now been updated (and are now Figure 8, formerly 4&6, and Figure 9, formerly 5). The averaging period/presentation of the model results now parallels the averaging period of the tables and discussion. Owing to this the color scales have also been updated and improved. These changes have resulted in the surrounding areas showing no change to slight increases. That said, the point that the reviewer raises as to the influence of non-local factors in the areas outside the urban

zones is still relevant. The model runs we have conducted in this study are not able to address this question as these factors were all kept constant throughout all the model runs. Therefore whatever influence non-urban factors might have, these should not be visible in any of the model runs. However, given the potential importance of non-local factors for the overall situation a discussion of these aspects has been included in the discussion to a greater degree than previous in section 3.5: Additional factors influencing changes in ozone.

21) If the authors believe that long-range transport of ozone and changes to background ozone are important contributors to the observed O3 increase in London, then they should include a discussion of how transported background O3 in Europe has actually changed from 1998 to 2008. Logan et al. [2012] have emphasized that background O3 in Europe has actually generally decreased over that period (see their Fig. 11); this must be discussed.

Response: We appreciate that the reviewer points out this literature on background ozone in Europe that is particularly relevant to this study as the time period considered is the same. That said, while long-term transport and changes in background ozone are no doubt relevant contributors to changes in European ozone, including London, the focus of this study was the evaluation of factors relevant for urban areas that influence local-scale ozone formation. These are necessarily superimposed on any changes in background ozone and a discussion of hemisphere, non-urban scale factors influencing ozone was included in the paper. The results from Logan et al., (2012) have been added to the discussion.

Minor issues: 1) p. 1288, line 25 - The authors state "... trends in peak ozone seem to be on the decline, ...". It is not the trends that are on the decline; it is the ozone concentrations that are on the decline. There are many such examples of careless wording, grammatical errors and other misusages of English in this paper. I will not attempt to identify them; the authors must conduct a careful copy editing of the paper to remove these problems.

Response: This instance has been corrected. The manuscript was also reviewed by a third party to hopefully catch any other grammatical errors, etc.

2) p. 1289, line 1 - Here is the first instance that the authors refer to "mean ozone". Here I assume they are discussing "annual, 24-hour mean". In each instance that this term is used in the paper, the time period over which the mean is calculated must be absolutely clear.

Response: this has been corrected to reflect the phrasing of the paper it was referencing. Other references to averaging periods have also been checked.

3) p. 1289, line 7 - Please give a brief description of the "the long-term ozone objective for human health"; including the time period over which the statistic is calculated, e.g. total annual exposure?

Response: These details have been included in the text. (ref: http://www.legislation.gov.uk/uksi/2010/1001/schedule/4/made)

4) When a reader examines Figure 1 it must be clear as to what the wind rose and O3 trends refer. Are these annual, 24-hour means?

Response: The figure caption has been updated to clarify that the ozone trends are from monthly average data, however, further details are referenced to the much more extensive discussion in the methods section. Clarification has also been added for the wind rose data, as well as a reference to further plots in the SI.

5) When a reader examines Table 1 it must be clear as to what quantities these trends refer: annual, 24-hour means?

Response: As with Figure 1, the table description has been updated to provide more detail, as well as a reference to further details provided in the methods section.

6) In Figure 2, the year of the measurements and model results should be given.

Response: This was an oversight. The figure caption has been updated to include the

necessary information.

7) The column headings in Table 2 are not clear for a reader who has not carefully read the modeling section. Please clarify. Also Table 2 should include model results for 1998 and 2008, as was done for the observations.

Response: We have added more information through the use of footnotes to clarify what is meant by the different columns in the table, as adding sufficient information in the header itself would not be feasible. As to including the model results for 1998 and 2008, these were omitted previously because for 1998 the modelled ozone is not and should not be comparable to the 1998 observations since the meteorology, etc are not from 1998. Furthermore, we present a comparison of 2008 observations and modelled data in Figure 2, as well as now having added further information and citations as to the model's ability to capture ozone in Europe and the UK. The focus of Table 2, and the analysis was to compare the relative change in ozone, not the absolute amounts. For this reason we have not added the absolute ozone concentrations from the model to the table. We have also removed the MR data from the table, as we found this to be distracting from the discussion, as it was never expected that MR would be representative of London, nor reproducible by the model, and was already not included in any of the 'London avg' values.

8) In Figure 5 the caption is not clear for a reader who has not carefully read the modelling section. Please clarify. Also the text boxes in the lower right corners of the 4 panels are not informative. They should be removed.

Response: Further information has been added to the caption of Figure 5 (now Figure 9) to clarify what is shown in each panel. The text boxes in the panels have also been removed.

9) p. 1300, line 3 - I think that the authors are referring to Fig. 5, not Fig. 6 here? It would also help to clarify the discussion if the panel of Fig. 5 that shows these results is specifically mentioned, i.e. bottom left I presume?

Response: This was an oversight, and has been corrected as suggested.

Reviewer 2

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 O3 is decreasing but 8 h average and background O3 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.

Response: The introductory paragraph has been updated and clarified to include information on different types of metrics and what they communicate about ozone. In addition, the local scale vs the regional scale aspect has been made clearer, also to communicate more clearly the interest or intention of our study.

Paragraph 2 needs to be more thorough. The provided description of the ozone chemistry is insufficient. Because the analysis aims to separate local O3 chemistry from transport/background effects on observed O3 abundances, a basic description of the nonlinear dependence of O3 production on its precursor species is warranted. Briefly describe the nonlinear dependence of O3 chemical production (PO3) on emissions. Discuss chemical loss of O3 to titration at high NO as a distinct process. State how these terms as well as transport and deposition impact measured O3 concentrations. A discussion of the nonlinear PO3 and O3 titration in the context of what O3 averaging (i.e. peak, daily mean, 8h) is under consideration would be useful to this analysis.

Response: While we agree with the reviewer that a more detailed discussion of ozone chemistry, production and loss processes are important, we aimed to augment the current discussion in the introduction without going through the basics of ozone chemistry that can be found in any textbook. The reasons for different types of trend analysis with respect to various metrics were included in the first paragraph.

Observations

Measured VOCs include “26 non-oxygenated non-methane C2-C8 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.

Response: We recognize that the 26 non-oxygenated non-methane C2-C8 HCs is a narrow subset of the VOC mix. We have expanded the discussion of OH reactivity and included further discussion that addresses some of these points. We have removed any scaling up of the VOCs using the inventory, as it results in unnecessary complication and does not add much to the discussion or results. As to the biogenics, only isoprene is included in those compounds that are measured, which is far from sufficient to capture the contribution of biogenic VOCs. To be clearer, the fact that isoprene was the only bVOC measured has now been explicitly mentioned in the methods section and mentioned in the discussion around ROH in section 3.2. As to the representativeness of the VOCs, we did not intend to suggest that measurements of VOCs from the

curbside site at Marylebone Road were representative of the London area as a whole, much less suburban or rural sites. Since the reviewer did not mention any specific text which gave that impression, we could not make a targeted change, however, we did substantially expand discussion of ROH in the manuscript, including the differences between the sites, as well as including comparisons to other urban areas. We also included discussion of missing reactivity and missing VOCs that should also address some of the short-comings/uncertainty resulting from the limited number of VOCs that are included in these measurements.

If ROH 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 ROH of the total VOC not then how it is defined it on page 1292 line 25? A definition of POCP is needed.

Response: In going through the reviews and revising the manuscript, it has become clear that any kind of scaling up of NMVOCs using the NAEI has not added to the paper and if anything has caused unnecessary confusion, as the reviewer rightly points out in this comment. It was decided to remove this aspect of the analysis.

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

Response: Significant detail has been added to the methods section including reasons for deseasonalizing e.g., NOx data and not VOC data. Further details on the methodology for deasonalizing have also been added.

What methodology is used to measure NO2? Is the technique selective for NO2? If not then the measured NO2 will be subject to positive interferences from higher oxides of nitrogen. Decreases in NOx 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 NOx. Could this influence the observed trends, i.e. cause the slower rates of decrease in NO2 compared to NO?

Response: The methodology used to measure NO2 is chemiluminescence using a heated Molybdenum convertor, which does create the issue of positive interference. However, this is the reference method of measurement as defined in the relevant EU directive (EN14211:2005). The monitoring sites follow approved methodologies to meet required criteria (MCerts). We have added an acknowledgement of this to the methods section, however, given that is the officially approved monitoring method, we are using the data as they are. This could potentially influence the observed trends, but then there would also need to be significant changes in the abundance of organic nitrates and nitric acid in the urban environment that would be changing at a rate significantly different from that of other NO2 emission sources, which given the reasons that are established for the slower rate of decrease in NO2 to NO, do not seem likely to be a large source of influence.

Page 1296, line 5: A reduction in congestion would decrease NOx emissions. This could happen on a fast timeline like the authors describe but would not change NO:NO2 unless accompanied by an adequately large change in O3 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).

Response: In response to comments to another reviewer, much of this discussion has been removed from the text. Also because if was correctly pointed out that calculating trends for data that is 5 years or less is not likely to yield a reasonable result. However, a more detailed discussion on NO2:NO ratios and the justification of what we used in the modelling and how these have changed over time has been added to the text in section 2.2.

Page 1296, line 28: This problem sounds surmountable.

Response: In response to comments from another reviewer, this line, as well as the discussion it references, has been removed. However, it is worth noting, that depending on how the trend analyses were conducted, a quantitative direct comparison is often not feasible, given different starting and ending points, whether the trend was calculated for ppbv/yr or in %/yr, etc. A general comparison of trends, taking these points into account, is however, definitely possible.

Modelling

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 PO3 that is incorrectly NOx suppressed.

Response: The information that we use for the NMVOC emissions is the NAEI, which is the official emissions inventory for the UK. It is always possible that the emissions are wrong, but we do not have enough data to suggest that and we are working under the assumption that it is the best available data. We have provided greater information in the manuscript of the emissions, through the inclusion of Figure C***, and greater discussion in the text. Comparison of measured and observed is unfortunately not possible here.

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

Response: Further information has been added to the description of the modelling experiments, including a line on purpose for each of the different runs. These explanations should ideally clarify the information that is targeted with each test.

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 NOx/VOC PO3 chemical regimes? Does each site allow a unique test of your model?

Response: The reviewer brings up some good points. In addition to the data coverage, the sites, with the exception of MR, should all provide fairly representative data of the urban area of London as a whole, given their classifications. Bloomsbury is a slight exception to this as an urban center site, which is more likely to be influenced by stronger local sources than the other sites classed as suburban or urban background. They should also all fall within the VOC-limited/NOx-saturated regime of the London area. They should theoretically offer similar views of the greater London area, and not diverging ones, with the exception again of Marylebone Road. Text has been added to the manuscript in section 2.3 to address these points.

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

Response: We chose to derive the NO:NO2 ratio and VOC speciation from the Marylebone Road site because for the experiment we are conducting to evaluate the change in emissions and other conditions over time, we wanted to use data that would be representative of 'fresh' emissions in London. As a curbside site, Marylebone Road is representative of such 'fresh' emissions. For this sensitivity study we also assume that emissions in the city are largely traffic dominated, as previous studies have shown (e.g., Parrish, et al., AE 2009). Text has been added to section 2.2 that explains in greater detail why this choice was made, as well as a justification for it.

Analysis of observations

Page 1298, lines 1–13: The authors need to provide a quantitative account of O3 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.

Response: The referenced page/line numbers reference end of section 3.2 on ROH and beginning of section 3.3 on emissions in the EMEP model. I am assuming that this was not the intent, but instead may refer to p. 1297 where a brief comparison to other reported ozone trends was made. We have expanded the discussion of the ozone trends here, and added further discussion of seasonal trends in an additional section (3.1.1) directly following the referenced section. Comparison with previous work has been expanded as well, but moved to a different section, now 3.1.2.

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

Response: This section has been expanded significantly to include a much more detailed discussion of ROH, including analysis of data from this manuscript, an additional figure, as well as comparison to other studies.

Page 1297, lines 15–19: I do not see how the decadal trend in ratio of NO2 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.

Response: As indicated in the responses to earlier comments, the estimated bottom-up account of total VOC reactivity has been dispensed with. The plot has been updated and that which is now included is based on measured data only. However, it is worth noting that the same result/trend is observed. Hopefully this change in approach addresses this issue.

Page 1297, line 19: Each factor affecting PO3 needs to be discussed. If a term cannot be constrained then the resulting uncertainty needs to be discussed.

Response: The reviewer is correct that much of the discussion surrounding the role of different factors affecting PO3 was not explicit enough. This has been amended in the aforementioned section, but also the subsequent discussion sections.

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

Response: The use of POCP has been removed from the manuscript.

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.

Response: The communication of this point has not been clear. We have amended the language of the sentence to hopefully make our point clearer, which is simply that the NO2:NMVOC contributions to reactivity observed at Marylebone Road were also observed at another site in London, and also in the Paris urban area. We are aware that the data from the other sites are much more limited, and did not mean to imply that the conditions at these sites evolved in a similar manner, which indeed cannot be concluded from the data at hand. But instead that there are similarities, which may indicate that the condition is not an anomaly for urban areas.

Sect. 3.3

Page 1298, line 11: The authors state that NO2 is decreasing as expected between 98 and 08 emissions but spend considerable time in Sect 3.1 explaining why increasing NO2 is observed.

Response: Much of the discussion in section 3.1 was focused on the one site (Marylebone Road) where an increasing trend in NO2 was observed. All other sites show decreasing NO2 trends. Much of this discussion about the particular pattern at Marylebone Road and the trend from this one site has been removed from this section, as suggested by another reviewer, since they found it distracting to the main points the paper is trying to communicate. This should also reduce confusion on this point. The decrease would be expected, given the trends at the vast majority of the sites around

London. This has been made clearer in the text.

The authors show that O3 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 O3 time series?

Response: In Figure 2, we show that the model reproduces ozone for 2008 data. Since this is a sensitivity study and we use the same meteorological conditions for all of the runs, we cannot compare the 1998 data with the 1998 model results that are produced here since they were run with 2008 meteorological conditions, which would not be an appropriate comparison. However, this model has been used to evaluate ozone over the UK and Europe previously and has been shown to reproduce ozone quite well; citations and information regarding the model's ability to reproduce ozone have been added to the manuscript.

Fig. 5: The information contained in the 4 panels is not clear to me. The authors show the modelled O3 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 O3 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 O3 in the London city center as they do across the rest of domain.

Response: The reviewer brings up a number of relevant points. First, the caption for Figure 5 (now Figure 9)has been improved and should now communicate more clearly what information the 4 panels present. Second, the model is designed to be run across the entire UK, and although it has much higher resolution than e.g, a regional model that encompasses all of Europe, it cannot reproduce fine, street-scale dynamic processes. Furthermore, we believe it is relevant to show London and the surrounding area, as the London plume affects a large area over southeast England as well. We

could zoom in/crop the plots to remove Scotland, but this does not seem necessary. Third, as to the model adequately describing O3 across England, in the original Figure 2 we compare a number of London sites, including those we would expect the model to reproduce (urban background, etc) and those we would not expect it to (Marylebone Road, curbside), for the reason mentioned above of not capturing street-level processes. In addition, we also show a comparison to ozone between modelled and measured at Mace Head, a background site that is typically used to compare with models, in which the comparison shows good agreement. Furthermore, the model has previously been used and validated for ozone over Europe and the UK (Vieno et al., 2010; Carslaw et al., 2011). These references and the explanation has been added to the manuscript. Finally, as to the bottom right panel and the NMVOCs. What this plot shows does not seem to have been made clearly, as the reviewer rightly pointed out, since it does not show emission changes in NMVOCs, but only the isolated effect of the change in their speciation. The figure caption has been updated to hopefully clarify this. In addition, another figure which shows the emissions used, and the difference in emissions for NOx and NMVOCs between the 1998 and 2008 basecase runs, has been added to the paper. This is shown now in Figure 7 (according to the new numbering). The change in total NMVOC emissions does indeed show larger differences over London and other urban areas, as the reviewer expected.

Sect. 3.4

Paragraph 1: The authors assign the O3 change not captured by the model to changes in the O3 of non-local origin. Uncertainty analysis of the modelled O3 is needed here.

Response: The model used here is very computationally expensive, as the version used here uses a sophisticated chemical mechanism. The model run time (6 days for a simulated year) somewhat limited the number of simulations that would be needed for a full uncertainty analysis. However, the EMEP model is used for EU policy applications and has been extensively validated and the performances are reported here: http://emep.int/publ/common_publications.html. We have added a discussion of the

model performance and uncertainty to section 2.2 to provide context to the discussion in section 3.4, including a number of references.

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.

Response: We do not understand what the reviewer means by this comment. However, if we assume that they are referencing differences in ozone trends inside and outside of the urban London area, the differences in trends from the surrounding sites relative to those in the city do indicate the influence of non-local effects. A complete analysis of the surrounding sites to the degree that was undertaken for the London sites is however beyond the scope of this paper.

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.

Response: The reviewer brings up an important point that should be addressed. Text has been added to this section to discuss the biogenic emissions. In the case of these model runs, biogenic emissions were not changed as the focus was on the anthropogenic emissions in the city. Therefore, changes in biogenic emissions could play an important role, however previous work has shown their contribution to still be relatively minor in the London area. However, it was acknowledged that the results here were limited to the effect of the change in speciation owing to only anthropogenic NMVOCs.

Page 1300, line 29: The authors need to separate NOx-suppressed PO3 from chemical loss to titration by NO both quantitatively and in their discussion of the NOx emissions effects.

Response: A much more in depth discussion of the different factors affecting ozone formation, including the role of photochemistry and chemical loss of O3 to titration by NO, has been included in the manuscript, specifically in section 3.4. Figures on the weekday-weekend effect, and seasonal evaluation of trends, as well as a more detailed discussion of the model results are now all included.

Page 1301, lines 1: Rather than mentioning the observation of a weekend effect in O3 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 O3 in London.

Response: A detailed analysis of the day-of-week observations have been included from the London dataset. This can now be found in section 3.4.1. It also includes an analysis of Ox (NO2 + O3), including a figure of these day-of-week patterns at 4 different London sites.

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

Response: The reviewers bring up a valid point that this discussion was disconnected from the rest of the manuscript. The discussion around the results and specifically these last 2 paragraphs has been significantly reworked, to include a more thorough analysis of previous trend analysis and factors influencing ozone that were not the subject of our model run study, and more relevant to regional/hemispheric ozone.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 1287, 2014.