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 μgm^{-3}) of the observed increase in urban (London) ozone (10 μgm^{-3}) in the UK from 1998 to 2008 is owing to factors of local origin, in particular, the change in NO:NO_2 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 μgm^{-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.

(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.)

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.

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.

3) The trend analysis reported in Table 1 should also be performed for NO_X = NO + NO_2. This is because measured concentrations of both NO and NO_2 are affected by changing total emissions, changing NO_2 to NO emission ratios, and changing ambient O_3 concentrations, while the sum is affected only by changing total emissions.

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 O_3, since decreasing titration by NO_X may be more important in winter compared to summer.

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.

6) p. 1293, lines 6-7 state "the NOx speciation (NO and NO_2) is also derived from observations at Marylebone road". Does this mean that the NO_2 to NO emission ratio was set equal to the observed ambient concentration ratio of NO_2 to NO? Surely, this cannot be correct, since the emitted NO_X will come into photostationary equilibrium with the sunlight and O_3 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.

7) p. 1296, lines 2-12 discuss two different trends of NO_2 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.

8) p. 1297, lines 1-13 - It is very important that the seasonal dependence of the O_3 trends be clearly discussed - see point 4) above.

9) Section 3.2 - This section concludes that the ratio of the reactivity of OH with NO_2 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."

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, NO_2, 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 NO_2 (and NO_X if my suggestion in 3) above is followed) to the measured trends reported in Table 1. This should indeed be shown.

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.

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?

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.

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.

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.

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.

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

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).

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.

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, O_3 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?

21) If the authors believe that long-range transport of ozone and changes to background ozone are important contributors to the observed O_3 increase in London, then they should include a discussion of how transported background O_3 in Europe has actually changed from 1998 to 2008. *Logan et al.* [2012] have emphasized that background O_3 in Europe has actually generally decreased over that period (see their Fig. 11); this must be discussed.

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.

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.

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?

4) When a reader examines Figure 1 it must be clear as to what the wind rose and O_3 trends refer. Are these annual, 24-hour means?

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

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

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.

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

Previous Review

This paper presents an analysis of ozone and its photochemical precursors in the United Kingdom, with a focus on the changes in their concentrations over the decade of 1998 to 2008. They "attributed just over half of the observed increase in urban ozone from 1998 to 2008 during the summer months to factors of local origin, the change in NO:NO2 ratio, NMVOC:NOx balance, and NMVOC speciation, as well as emission reductions. In NOx saturated areas, 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 increase in ozone that was observed is attributed to factors that are not controllable locally, such as (long-term) transport of ozone, changes in background ozone, and meteorological variability."

However, this paper's central idea that local NO emissions can reduce ozone in urban areas is certainly not original in this paper (e.g., *National Academy of Sciences,* 1991), and is widely appreciated in the air quality community. It is also clear that ozone, when considered from the perspective of seasonal, 24-hour averages, is generally depressed in UK urban areas compared to air flowing into the UK from the North Atlantic Ocean (e.g. compare summertime ozone averages in Table 2 of this paper for the London area to those reported for Mace Head, Ireland by *Simmonds et al.,* 2004). And it is widely recognized that reducing NO emissions often increases urban ozone when characterized as seasonal, 24-hour averages. Hence, the title of this

paper is simply a new term for a well-known feature of atmospheric pollution.

A novel feature of this paper is an attempt to apportion the observed increase of ozone in London between local and other influences. In essence the authors attempt this apportionment by comparing the observed change in ozone to the change in ozone predicted by model simulations of the photochemical environment of London in 1998 and in 2008. They find that their model results capture "just over half of the observed increase" and they therefore attribute the "remaining increase in ozone that was observed" to other factors that were not incorporated in the model. However, I do not believe the conclusions from that attempt are persuasively presented in this paper due to two major flaws discussed below. In my view each of these flaws renders the paper unsuitable for publication.

First, I do not believe that the current state of photochemical modeling is adequate to quantitatively calculate the small ozone change that has occurred over the decade in question. One problem is the lack of accurate emission inventories for the two years of modeling. Figure 2 of the paper shows that the emissions in the inventory did not change at the same rate as ambient concentrations observed in emission dominated regions, so problems in the inventory must be suspected. A second problem is that the authors compare summertime mean 24-hour ozone between the model and the measurements. It is very difficult for photochemical models to accurately calculate 24-hour means, because (among other problems) results are strongly dependent upon the diurnal evolution of the planetary boundary layer (PBL), which models are notoriously poor at reproducing. The net effect of changes in NO emissions will depend strongly on that PBL evolution. To persuasively demonstrate that the model calculations are reliable would entail detailed comparisons of modeled and measured ozone on diurnal, day of the week and seasonal time scales, as well as in the vertical through the PBL. When these detailed comparisons have been made, only then can we confidently accept the model results. Such a comparison is appropriate for a specialty journal, but not for inclusion in this journal, but the comparison must be available to the interested reader.

Second, the paper is very poorly written so that exactly what was done is impossible for me to understand. Examples of this problem include:

- The first three columns of Table 2 give observations of ozone in 1998, ozone in 2008 and Δ ozone, yet the third column is not equal to the difference of the first two. I spent some time attempting to understand what was going on, but was unable to do so.
- The authors do not specify units in Table 1 or Figure 1, and do not clearly explain their tests of significance.
- The authors seem to give inconsistent comparisons, switching between annual averages, summertime averages and average summertime daily maximum. Each of these measures depends sensitively and differently to factors that affect ozone. The authors must clearly and consistently present their comparisons.
- Ambient data from Marylebone Road measurements were used to guide aspects of the emission inventories used in the modeling, but then data from that site were excluded from comparison with the model. Certainly this exclusion requires strong justification.
- Evidently the $NO:NO_2$ emission ratios included in the model were based upon Marylebone Road measurements, but since NO, NO_2 and O_3 reach a photostationary steady state within about a minute following emission to the atmosphere, this approach is likely to be quite misleading.

In summary, in my judgment this paper needs much work before it is suitable for publication, and since it needs much detailed comparisons between model results and measurements, it is much more suitable for a specialized journal ....

References

Logan, J. A., et al. (2012), Changes in ozone over Europe: Analysis of ozone measurements from sondes, regular aircraft (MOZAIC) and alpine surface sites, *J. Geophys. Res., 117*, D09301, doi:10.1029/2011JD016952.

National Academy of Sciences, 1991. Rethinking the Ozone Problem in Urban and Regional Air Pollution. National Academy Press, Washington D.C.

Simmonds, P.G., Derwent, R.G., Manning, A.J., Spain, G., 2004. Significant growth in surface ozone at Mace Head, Ireland, 1987–2003. Atmospheric Environment 38, 4769–4778.