

Review of " Ozone Response to Emission Reductions in the Southeastern United States" by Charles L. Blanchard and George M. Hidy

MS Number: acp-2017-534

Summary:

The paper presents some useful analysis of a very valuable data set. The SEARCH data cover more than 2 decades of measurements made at eight sites in the southeastern U.S., and certainly deserve careful analyses from many perspectives. Some of that analysis is presented in this paper, but major portions of the analysis are incorrect, and are consequently misleading. Major issues that require attention are detailed below, followed by listing of more minor issues with suggestions for improvement. I suggest that this paper not be accepted before it has been extensively revised to address the issues detailed below.

Major issues:

- 1) In the abstract the authors conclude that "The O₃ declines are less than proportional to the decreases in NO_x emissions: emissions decreased by ~60% and O₃ maxima declined ~30 – 35% at rates averaging ~1 ppbv y⁻¹." However, the authors neglect to consider the contribution of transported background O₃ contributions to the O₃ maxima. When this contribution is properly considered, the declines will be much more nearly proportional (see comment 4) below for more details).
- 2) In the abstract the authors also conclude that "Ozone production efficiency (OPE, molecules of O₃ produced per molecule of NO_x oxidized) increased between 1999 and 2014, which affected the magnitude of the O₃ response to NO_x emission reductions by partially offsetting precursor decreases and contributing to the nonlinear O₃ response." However, the OPE analysis presented is flawed (see comment 7) below for more details), and this conclusion is simply not correct. It must be removed.
- 3) The abstract ends with the conclusion that "The results suggest increasing responsiveness of O₃ to NO_x, but the effectiveness of ongoing NO_x emission reductions will depend on the balance between changes in observed OPE and ambient NO_x in the context of changes in anthropogenic emissions of volatile organic compounds (VOC). This conclusion is not supported by valid analysis in this paper; it must also be removed.
- 4) On pg. 8 the authors make two observations with regard to figure 2. First, "O₃ mixing ratios are declining toward nonzero values, as indicated by the statistically-significant ($p < 0.0001$) intercepts of ~45 – 50 ppbv." Second, "the O₃ declines are less than proportional to the decreases in NO_x emissions, as indicated by the ~60% emission reduction and ~30 – 35% O₃ declines shown in Figure 2, about equivalent to the national trends discussed in Section 2.2". These two observations are closely connected and should be discussed further.

First, the intercepts can be reasonably interpreted as U.S. background O₃ contributions (i.e., the O₃ concentrations that would be present in the absence of U.S. anthropogenic precursor emissions) to these O₃ concentrations. The derived intercepts of ~45 – 50 ppbv can be compared to other estimates of U.S. background O₃ concentrations. *Berlin et al.* [2013] estimate mean regional background O₃ concentrations of 48 ppbv to 59 ppbv on exceedance days in the Houston TX area. However, these estimates include O₃ contributions from transport to the area from other regions of the U.S., and thus are higher than true U.S. background O₃ concentrations. It should also be noted that these estimates for Houston

exceedance days are higher than the regional average of all summer days. *Parrish et al.* [2017a] note that the highest ozone design values (i.e., the 3 year running mean of the 4th highest 8-hour average O₃ concentration) in Southern California air basins are converging toward of limit of 62.0 ± 1.9 ppb, which they identify as the ozone design values that would result from only U.S. background ozone concentrations. The California background ozone concentrations are higher than in Texas or the Southeastern United States discussed in the present paper due to differences in state orography, site altitudes and proximity to major areas of surface impact from stratospheric intrusions. Such comparisons should be discussed in the present paper.

Second, it would be more informative to compare the percentage declines in NO_x emissions to the percentage declines in O₃ after subtracting the intercepts; such a comparison would give significantly larger relative O₃ reductions, and these higher results would be closer in magnitude to the relative reductions in NO_x emissions; this comparison would more faithfully reflect the reduction in the anthropogenic contribution to observed O₃ concentrations. For example, *Parrish et al.* [2017a] find that the ozone enhancement above background in Southern California has decreased with an e-folding time of 21.9 years, which corresponds to a decrease of 4.5%/yr, larger than the value of 2.8%/yr given by *Pollack et al.* [2013] as cited by the authors. This difference arises because *Pollack et al.* [2013] did not subtract the background before deriving the relative rate of decrease.

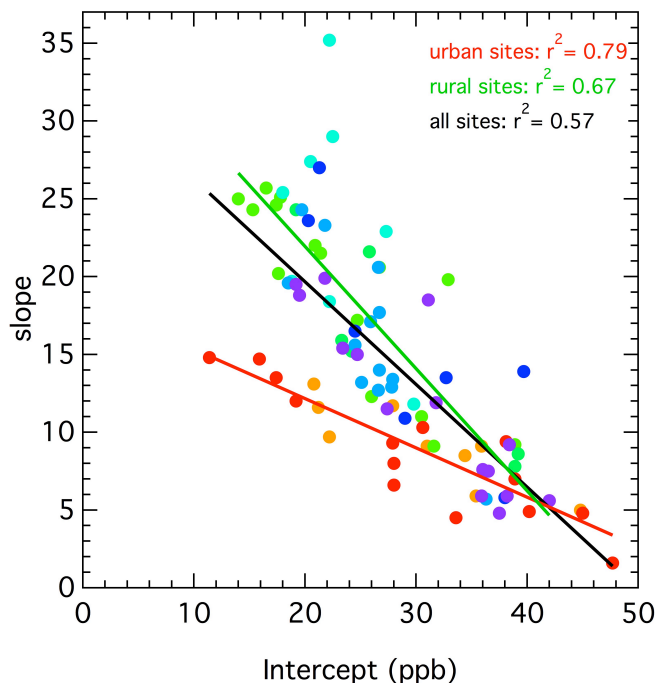
Considering O₃ trends after background subtraction makes a substantial difference. In Southern California this approach implies that the anthropogenic enhancement of ozone (the only pollution contribution that is within the control of U.S. policy makers) has decreased by a factor of 5 from 1980 to 2015. This factor is larger than generally appreciated, and is an important success story for air quality improvement efforts in the U.S. that deserves wider recognition. It is also notable that this rate of decrease is between the rates of decrease of ambient VOCs and NO_x (7.3% yr⁻¹ and 2.6% yr⁻¹, respectively, 1960 – 2010) in Southern California, as cited by the present authors. This same consideration of the change in the anthropogenic enhancement of ozone should be presented in this paper for the Southeastern U.S. I realize that the references cited in Table S2 did not subtract the U.S. background concentration before calculating the tabulated relative ozone decreases; this likely explains much of the regional difference between Southern California and the Southeastern U.S. I strongly recommend that this subtraction be done and discussed in this paper.

- 5) The sentence beginning on Pg. 9, line 2 ("Both EPA (Figure 2) and SEARCH (Figure 3) data suggest that O₃ mixing ratios increased during the 1990s, then began declining.") suggests that the trends in Figure 3 should be calculated only after the increase had ended, i.e., beginning in the year ~2000. When this is done, some of the trends (i.e., CTR, YRK and OAK) will be steeper, and there may be better agreement among the trends at the different sites.
- 6) The correlations shown in Figure 5 are misleading, and this figure should not be included without extensive modification. One major problem is that the figure combines wintertime data, when O₃ concentrations may be reduced below those in transported background air due to titration by NO emissions, with summertime data, when O₃ concentrations are increased above those in transported background air due to photochemical O₃ production. The figure should either include data from one season only, or plot O_x (= O₃ + NO₂) concentrations, which are much less sensitive to the NO titration, instead of O₃ only concentrations. The

SEARCH data are somewhat unique in having simultaneous high quality O₃ and NO₂ data, and this analysis should take advantage of this uniqueness. This plot may be further confused by wintertime conversion of NO_x to NO_z through NO₃ and N₂O₅ chemistry, which destroys rather than produces O₃.

7) Section 4.4 attempts to quantify ozone production efficiency (OPE) from observations, but this entire discussion must be rethought. There may be something of value in the extensive analysis that the authors performed, but the current discussion is simply not correct. Specific difficulties include:

- Ozone is quite low (≤ 20 ppb) at low NO_z concentrations in figures 8 and 9; this immediately identifies a clear problem in the analysis. The observationally based determination of OPE implicitly assumes that "background air" contains zero NO_z concentrations and O₃ concentrations representing regional background transported into the region. Variations of O₃ concentrations transported into the region must be negligible compared to the O₃ produced within the region or locally. That is simply not the case here. With few exceptions, all of the O₃ concentrations in Figure 9 are < 65 ppb. *Berlin et al.* [2013] show that regional background O₃ concentrations varied between ~ 10 and 70 ppb in the Houston area in the mid 2000s. Thus, it is conceivable that Figure 8 and 9 (particularly the latter) are dominated by O₃-NO_z relationships in the transported regional background, and provide little or no information regarding ozone formation within the SEARCH region.
- Figure 9 gives linear fits of observed O₃ vs NO_z for one year, and Table S4 gives the results for all years of data. The figure below shows the relationship between the derived slopes and intercepts for all years and all sites in Table S4. If the slopes were indeed providing information about the local and regional photochemistry, they would be expected to be independent of the intercepts, which reflect the regional background; such independence is clearly not seen. For the two urban sites (BHM and JST) the intercepts account for almost 80 of the variability in the slope.
- The paragraph beginning on pg. 12, line 7 attempts to account for the influence of depositional loss of NO_z on derived OPE values, and the influence of varying background O₃ concentrations. Unfortunately, the three different methods employed, yield quite different OPE values (Figures S15 – 17). Also, the results do not make good physical sense; e.g. how can OPE be near zero in 2001 at JST? Thus, this discussion increases the skepticism with which the entire analysis must be considered.



- The paragraph beginning on pg. 13, line 4 compares the intercepts of year-specific regressions for 2013 (~20 ppb O₃) with other estimates of background levels. However, this comparison is not valid. Some of the references cited (Lefohn et al., 2014; Dolwick et al., 2015) are modeling studies that discuss U.S. background O₃ according to the EPA definition, which is the O₃ concentration that would exist if all U.S. anthropogenic emissions of ozone precursors were reduced to zero. Others (Chan and Vet, 2010) report observationally-based estimated baseline O₃ concentrations in the absence of any continental influences. These two concepts are very different from regional background O₃, i.e. the O₃ concentration actually transported into the region of interest, including from other U.S. regions that are rich in anthropogenic emissions of ozone precursors. A comparison with the work of *Berlin et al.* [2013] is much more appropriate for discussion of the SEARCH region.
 - In Section 4.4.2 the authors compare their results with cited work from the published literature. Many of the references cited give results from studies that suffer from the same problems as plague the present work. For example *Travis et al.* (2016) follow much the same approach as the present paper - they interpret the slope of the correlations of Ox vs. NOz as OPE with no analysis to ensure that the low Ox-low NOz air and the high Ox-high Oz air actually represent similar background Ox and NOz concentrations, to which varying amounts of precursors were injected and subsequently photochemically processed. Reliable analysis of OPEs requires careful plume analysis, similar to that presented in *Neuman et al.*, 2009 (a reference that is not cited in the present paper). One approach to deriving OPEs from surface site data is given by *McDuffie et al.*, 2009 (a reference that the authors cite, but do not discuss the OPE results therein.) The references to *Liu et al.* (1987) and *Lin et al.* (1988) are not germane to the present discussion, as these results are from a very early global model, and report the total ozone produced when all VOCs, including only relatively unreactive VOCs are completely oxidized over months.
 - Finally, a very simple argument makes it quite clear that something is amiss in the entire OPE analysis. Section 4 begins with a discussion of trends in NOx emissions, emphasizing a reduction of a factor of ~3 between 1996 and 2014. Figure 10 suggests that OPE has increased by a factor of ~5. If both of these findings were correct, then O₃ concentrations, at least from local and regional production, would have increased, not decreased, over this period. Yet the authors note that O₃ concentrations have in fact decreased. There is a critical inconsistency buried in this analysis
 - Section 4.4.3 is highly speculative, and based upon inaccurate OPEs as discussed above. It should be eliminated in its entirety, or at least extensively modified if the issues listed above can be effectively addressed.
- 7) The Conclusions section must be revised consistent with the revisions needed to address the above issues.

Minor issues:

- 1) Line 11: typo - "... in in Alabama and Georgia."
- 2) In my opinion Figure 1a would be more informative as a semi-log plot. Then the NOx emission and nitrate deposition traces would parallel each other, and the linear slope of the

log-transformed data would be directly proportional to the % decrease/yr. If the NO_x emissions were plotted on the right axis and the deposition data on the left with the same factor change on each axis, but the offset on each axis chosen properly, then the emissions and deposition curves would be approximately superimposed.

- 3) Pg. 8, lines 18-19: At least the SEARCH downward trends in mean annual HNO₃ concentrations in %/yr that can be derived from Figure S4 should be compared to the corresponding trends in NO_x emission and nitrate deposition. (The EPA HNO₃ trends do not seem to make good physical sense.) Figure S4 also would be more informative as a semi-log plot.
- 4) The de Gouw et al., 2014 reference is omitted from the References list.
- 5) I do not understand the sentence beginning on Pg. 8, line 23: "Spatial variability of the annual 4th-highest daily peak 8-hour O₃ mixing ratios has decreased (Figure 2), consistent with an analysis of data from a larger number of U.S. and European locations (Paoletti, et al., 2014)." Figure 2 has no direct information regarding spatial variability. It is true that the spread in the percentiles of the 4th highest O₃ concentrations has decreased, but this is only to be expected as the absolute magnitude of the anthropogenic ozone enhancement has decreased. In terms of absolute ozone concentration, then the spatial variability is expected to have decreased simply because all of the region is approaching the U.S. background O₃ concentration, which is expected to have small spatial variability in the Southeastern U.S. This sentence should be more clearly explained.
- 6) I suggest that the sentence beginning on Pg. 9, line 7 be reworded: "The meteorological factors having the strongest influence on daily peak 8-hour O₃ mixing ratios at SEARCH sites are daily maximum temperature and mid-day relative humidity (RH), whose variations cause daily peak 8-hour O₃ mixing ratios to vary by ~ ±30 percent from mean peak 8-hour O₃ mixing ratios (Blanchard et al., 2014)." I assume that these results are simply correlations, without proof of cause; thus the sentence should read something like: "The meteorological factors correlating most strongly with daily peak 8-hour O₃ mixing ratios at SEARCH sites are daily maximum temperature and mid-day relative humidity (RH), with variations of daily peak 8-hour O₃ of ~ ±30 percent from mean peak 8-hour O₃ mixing ratios (Blanchard et al., 2014)."
- 7) The sentence beginning on Pg. 9, line 24 is likely misleading: "Background O₃ may also represent an increasing absolute contribution in our study area, as multiple studies have demonstrated increasing trends in global background O₃ mixing ratios." The cited studies have all focused on northern mid-latitudes, where the background O₃ mixing ratios have indeed increased. However, Parrish et al. [2017b] show that increase generally ended in the early to mid 2000s. Further, Berlin et al. [2013] show that baseline ozone concentrations in air flowing into Texas from the Gulf of Mexico have not changed significantly over the 1990-2010 period. It is likely that the Gulf of Mexico inflow better represents the background ozone affecting the Southeastern U.S., which is the subject of this paper.
- 8) The sentence on Pg. 10, lines 13-16 clearly refers to data over the full year. It would be more informative to include the % of the VOC reactivity due to isoprene just for the summer months when both the high isoprene and high ozone concentrations occur. Similarly, the alkene and aromatic contributions to average VOC OH reactivity for the high ozone summer season should be contrasted with the annual average numbers that are given.

References

Berlin, S.R., A.O. Langford, M. Estes, M. Dong, and D.D. Parrish (2013), Magnitude, decadal changes and impact of regional background ozone transported into the greater Houston, Texas area, *Environ. Sci. Technol.*, 47(24), 13985-13992, doi:10.1021/es4037644.

Neuman, J. A., et al. (2009), Relationship between photochemical ozone production and NO_x oxidation in Houston, Texas, *J. Geophys. Res.*, 114, D00F08, doi:10.1029/2008JD011688.

Parrish, D. D., Young, L. M., Newman, M. H., Aikin, K. C., & Ryerson, T. B. (2017a). Ozone design values in Southern California's air basins: Temporal evolution and U.S. background contribution. *Journal of Geophysical Research: Atmospheres*, 122. <https://doi.org/10.1002/2016JD026329>

Parrish, D. D., Petropavlovskikh, I., & Oltmans, S. J. (2017b). Reversal of long-term trend in baseline ozone concentrations at the North American West Coast. *Geophysical Research Letters*, 44. <https://doi.org/10.1002/2017GL074960>