

Interactive comment on “Ozone Response to Emission Reductions in the Southeastern United States” by Charles L. Blanchard and George M. Hidy

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We thank the reviewer for helpful suggestions and address the reviewer's questions in the following paragraphs.

The SEARCH measurements of NOy were designed to capture particulate nitrate and organic nitrates, as well as NO, NO₂, HNO₃, and other oxidized nitrogen species. The NOy sampler derives from the ESE instrument discussed in Williams et al. (1998), which was one of five instruments for which measurements of NOy reproduced the sum of separately measured NOy species. Additional testing in 2013 showed that SEARCH NOy measurements agreed with the sum of measured mixing ratios of NO,

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NO₂, HNO₃, particulate nitrate, alkyl nitrates, and peroxy–alkyl nitrates (Hidy et al., 2014). The NO_y measurements have therefore been shown to capture oxidized nitrogen species near both the beginning and the end of the study years. As described in the manuscript, the method for measuring NO₂ is NO₂-specific, but over time the instruments utilized three different types of lamps for the photolytic conversion of NO₂ to NO. We therefore tested for biases in the O₃-NO_z relationships by determining O₃-HNO₃ relationships as described, and concluded that similar temporal changes occurred in both sets of relationships.

We concluded that our observed increases in the slopes of summer O₃ versus NO_z did not result from variations in background O₃ based on a set of auxiliary analyses that we provided. Rather than generating more auxiliary analyses, we argue here that other studies sufficiently support and justify our conclusions. O₃ decreases driven by reductions of NO_x emissions between 1980 and 2014 were most pronounced in the southeastern US, where the seasonal onset of biogenic isoprene emissions and NO_x-sensitive O₃ production occurs earlier than in the northeastern U.S. (Lin et al., 2017). Lin et al. (2017) show that rising NO_x emissions in Asia have increased modeled North American background O₃ levels (based on model simulations with zero North American emissions) by ~0.2 ppbv yr⁻¹ in the southeastern U.S. in summer. The model-predicted increase in background O₃ in the southeastern U.S. is too small to be a systematic cause of our observed twofold (or more) increase in the slopes of summer O₃ versus NO_z. Moreover, the actual O₃ levels occurring in the southeastern U.S. during our study period would have been influenced by transport of air masses affected by non-zero North American emissions occurring upwind of our study area, i.e., by regional background, whose changes likely differ from changes in North American background.

Observed trends in the 5th percentile O₃, have previously been used as indicators of changes in regional or continental background O₃ (e.g., Wilson et al., 2012). The 5th percentile peak daily 8-hour O₃ mixing ratios decreased during summer at rural sites throughout the southeastern U.S. between 1988 and 2014 (Lin et al., 2017). By this

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measure, background O₃ levels were not increasing in the southeastern U.S. during our study period and therefore could not have introduced a positive bias in observed ozone production efficiency (OPE, estimated as the slopes of summer O₃ versus NO_x). The trend in the 95th percentile summer peak daily 8-hour O₃ mixing ratios in the southeastern US reported by Lin et al. is \sim -0.8 to -1.8 ppbv yr⁻¹, with downward trends occurring in other seasons as well. Our findings are comparable: between 1999 and 2014, the highest peak daily 8-hour O₃ mixing ratios occurring each month) declined at all SEARCH sites at statistically significant ($p < 0.01$) rates averaging \sim 1 ppbv yr⁻¹ (our Figure 3).

Anthropogenic emissions and long-range transport (long-range tropospheric + stratospheric) O₃ each accounted for about 40% (15 – 20 ppbv) of model-predicted O₃ below 1 km altitude at Huntsville, AL, during June 2013, while long-range transport accounted for \sim 80% of model-predicted O₃ above 4 km altitude (Johnson et al., 2016). Using ozonesondes that are launched on a typically weekly schedule, vertical O₃ mixing ratio profiles have been determined by the University of Alabama in Huntsville, Alabama, since 1999 (Newchurch et al., 2003; Johnson et al., 2016; University of Alabama, 2017; NOAA, 2017). We obtained the ozonesonde data (University of Alabama, 2017; NOAA, 2017) and identified the following statistically significant trends in the lower layers that are relatively more influenced by local and regional emissions according to Johnson et al. (2016): -0.25 ± 0.11 ppbv y⁻¹ ($p < 0.05$) at 0.5 km, -0.40 ± 0.10 ppbv y⁻¹ ($p < 0.0001$) at 1 km, -0.42 ± 0.09 ppbv y⁻¹ ($p < 0.0001$) at 2 km, and -0.57 ± 0.13 ppbv y⁻¹ in monthly averages of O₃ measurements made throughout the interval 1 – 2 km ($p < 0.001$). At higher altitudes where Johnson et al. (2016) predicted that long-range transport is the dominant source of O₃, no trends occurred: 0.06 ± 0.08 ppbv y⁻¹ ($p > 0.1$) at 4 km and 0.09 ± 0.19 ppbv y⁻¹ ($p > 0.1$) at 8 km. The Huntsville ozonesonde data support our conclusion that changes in observed OPE are not biased by trends in transport of background O₃.

We suggest revising the second paragraph of Section 4.4.2 as follows: “The increase

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in OPE with decreasing ambient NO_x and NO_z is also consistent with computations by Liu et al. (1987), which show relatively constant summer OPE of ~ 7 - 10 for ambient NO_x exceeding ~ 7 ppbv and increases in OPE to ~ 20 as NO_x declines from ~ 7 to ~ 1 ppbv. While the numerical results of the modeling calculations by Liu et al. (1987) are specific to the modeled conditions, increasing OPE results from multiple factors that are pertinent to other conditions, such as radical reactions involving VOCs and NO_x (Lin et al., 1988). This revision eliminates reference to model-predicted OPE at lower NO_x mixing ratios. The SEARCH data do not provide an observational test of Liu et al.'s (1987) model prediction that OPE increases to ~ 60 - 80 as NO_x declines to ~ 0.1 ppbv to ~ 0.01 ppbv, because fewer than 0.2% of the 2 p.m. SEARCH NO_x mixing ratios were below 0.1 ppbv.

The first paragraph of Section 4.4.3 can be shortened to read: "Where NO_x limits reaction rates, O₃ production is the product of OPE and ambient NO_x mixing ratios as determined for specific ambient conditions (Liu et al., 1987), so O₃ reductions depend on changes in both OPE and NO_x. At present, there is no clear indication from the SEARCH data that OPE will continue to increase, level off, or begin decreasing. The post-1990s O₃ trend provides one guide to future average rates of O₃ reduction in the sense that the rates of O₃ reduction during the next decade are unlikely to deviate dramatically from those of the recent past. This result would be expected if OPE remains roughly constant or decreases somewhat, as indicated in Figure 10 for the years since about 2009. Previous work indicates that VOC reactivity and O₃ losses contribute to nonlinearity; at ambient NO_x mixing ratios less than ~ 0.4 ppbv, O₃ loss suppresses OPE, and below ~ 80 pptv NO_x, OPE becomes negative (Lin et al., 1988)."

The importance of isoprene emissions for ozone production in the southeastern U.S. is well established (e.g., Chameides et al., 1988; Chameides and Cowling, 1995; Frost et al., 1998; Starn et al., 1998; Wiedinmyer et al., 2006; Zhang et al., 2014; Lin et al., 2017) and requires no further analysis. In our view, the suggested evaluation of reactivity utilizing the Carter (1994) MIR and MOIR O₃ reactivity scales would be limited by

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the availability of data, would not provide new insight, and would not contribute to our assessment of the relationship between O₃ and NO_x in the southeastern U.S. Panel (d) of Figure 6, intended to be illustrative, can be eliminated if it is a distraction. We can simply reference the literature on isoprene reactivity and the significance of seasonal isoprene emissions in the Southeast.

We suggest rewording the second half of the abstract as follows: “Between 1996 and 2015, annual 4th-highest daily peak 8-hour O₃ mixing ratios at EPA monitoring sites in Georgia, Alabama, and Mississippi exhibited statistically-significant ($p < 0.0001$) linear correlations with annual NO_x emissions in those states, decreased by $\sim 30\%$ on average, and declined at rates averaging ~ 1 ppbv y⁻¹. Ozone production efficiency (OPE, molecules of O₃ produced per molecule of NO_x oxidized) increased by factors of ~ 2 or more between 1999 and 2014, which partially offset the $\sim 60\%$ NO_x emission reductions and limited the O₃ decreases. The results suggest increasing responsiveness of O₃ to NO_x as NO_x emissions decline, 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).”

The correct statement in the caption of Figure 2 should be “a) trends (ranges denote 90th and 10th percentile site’s values).”

We will shorten Section 2.1 (background information on atmospheric chemistry), relying on textbook and research reviews for details. We agree that this material appears extensively in the literature and does not need to be expanded in our manuscript, which is not intended as a comprehensive review.

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