

## ***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 NO<sub>y</sub> were designed to capture particulate nitrate and organic nitrates, as well as NO, NO<sub>2</sub>, HNO<sub>3</sub>, and other oxidized nitrogen species. The NO<sub>y</sub> sampler derives from the ESE instrument discussed in Williams et al. (1998), which was one of five instruments for which measurements of NO<sub>y</sub> reproduced the sum of separately measured NO<sub>y</sub> species. Additional testing in 2013 showed that SEARCH NO<sub>y</sub> measurements agreed with the sum of measured mixing ratios of NO,

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NO<sub>2</sub>, HNO<sub>3</sub>, particulate nitrate, alkyl nitrates, and peroxy-alkyl nitrates (Hidy et al., 2014). The NO<sub>y</sub> 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 NO<sub>2</sub> is NO<sub>2</sub>-specific, but over time the instruments utilized three different types of lamps for the photolytic conversion of NO<sub>2</sub> to NO. We therefore tested for biases in the O<sub>3</sub>-NO<sub>z</sub> relationships by determining O<sub>3</sub>-HNO<sub>3</sub> 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 O<sub>3</sub> versus NO<sub>z</sub> did not result from variations in background O<sub>3</sub> 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. O<sub>3</sub> decreases driven by reductions of NO<sub>x</sub> emissions between 1980 and 2014 were most pronounced in the southeastern US, where the seasonal onset of biogenic isoprene emissions and NO<sub>x</sub>-sensitive O<sub>3</sub> production occurs earlier than in the northeastern U.S. (Lin et al., 2017). Lin et al. (2017) show that rising NO<sub>x</sub> emissions in Asia have increased modeled North American background O<sub>3</sub> levels (based on model simulations with zero North American emissions) by ~0.2 ppbv yr<sup>-1</sup> in the southeastern U.S. in summer. The model-predicted increase in background O<sub>3</sub> 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 O<sub>3</sub> versus NO<sub>z</sub>. Moreover, the actual O<sub>3</sub> 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 O<sub>3</sub>, have previously been used as indicators of changes in regional or continental background O<sub>3</sub> (e.g., Wilson et al., 2012). The 5th percentile peak daily 8-hour O<sub>3</sub> 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 O<sub>3</sub> 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 O<sub>3</sub> versus NO<sub>z</sub>). The trend in the 95th percentile summer peak daily 8-hour O<sub>3</sub> mixing ratios in the southeastern US reported by Lin et al. is  $\sim -0.8$  to  $-1.8$  ppbv yr<sup>-1</sup>, with downward trends occurring in other seasons as well. Our findings are comparable: between 1999 and 2014, the highest peak daily 8-hour O<sub>3</sub> mixing ratios occurring each month) declined at all SEARCH sites at statistically significant ( $p < 0.01$ ) rates averaging  $\sim 1$  ppbv yr<sup>-1</sup> (our Figure 3).

Anthropogenic emissions and long-range transport (long-range tropospheric + stratospheric) O<sub>3</sub> each accounted for about 40% (15 – 20 ppbv) of model-predicted O<sub>3</sub> below 1 km altitude at Huntsville, AL, during June 2013, while long-range transport accounted for  $\sim 80\%$  of model-predicted O<sub>3</sub> above 4 km altitude (Johnson et al., 2016). Using ozonesondes that are launched on a typically weekly schedule, vertical O<sub>3</sub> 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):  $-0.25 \pm 0.11$  ppbv y<sup>-1</sup> ( $p < 0.05$ ) at 0.5 km,  $-0.40 \pm 0.10$  ppbv y<sup>-1</sup> ( $p < 0.0001$ ) at 1 km,  $-0.42 \pm 0.09$  ppbv y<sup>-1</sup> ( $p < 0.0001$ ) at 2 km, and  $-0.57 \pm 0.13$  ppbv y<sup>-1</sup> in monthly averages of O<sub>3</sub> 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 O<sub>3</sub>, no trends occurred:  $0.06 \pm 0.08$  ppbv y<sup>-1</sup> ( $p > 0.1$ ) at 4 km and  $0.09 \pm 0.19$  ppbv y<sup>-1</sup> ( $p > 0.1$ ) at 8 km. The Huntsville ozonesonde data support our conclusion that changes in observed OPE are not biased by trends in transport of background O<sub>3</sub>.

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<sub>x</sub> and NO<sub>z</sub> is also consistent with computations by Liu et al. (1987), which show relatively constant summer OPE of  $\sim 7 - 10$  for ambient NO<sub>x</sub> exceeding  $\sim 7$  ppbv and increases in OPE to  $\sim 20$  as NO<sub>x</sub> declines from  $\sim 7$  to  $\sim 1$  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<sub>x</sub> (Lin et al., 1988).” This revision eliminates reference to model-predicted OPE at lower NO<sub>x</sub> mixing ratios. The SEARCH data do not provide an observational test of Liu et al.’s (1987) model prediction that OPE increases to  $\sim 60 - 80$  as NO<sub>x</sub> declines to  $\sim 0.1$  ppbv to  $\sim 0.01$  ppbv, because fewer than 0.2% of the 2 p.m. SEARCH NO<sub>x</sub> mixing ratios were below 0.1 ppbv.

The first paragraph of Section 4.4.3 can be shortened to read: “Where NO<sub>x</sub> limits reaction rates, O<sub>3</sub> production is the product of OPE and ambient NO<sub>x</sub> mixing ratios as determined for specific ambient conditions (Liu et al., 1987), so O<sub>3</sub> reductions depend on changes in both OPE and NO<sub>x</sub>. 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 O<sub>3</sub> trend provides one guide to future average rates of O<sub>3</sub> reduction in the sense that the rates of O<sub>3</sub> 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 O<sub>3</sub> losses contribute to nonlinearity; at ambient NO<sub>x</sub> mixing ratios less than  $\sim 0.4$  ppbv, O<sub>3</sub> loss suppresses OPE, and below  $\sim 80$  pptv NO<sub>x</sub>, 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 O<sub>3</sub> 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 O<sub>3</sub> and NO<sub>x</sub> 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 O<sub>3</sub> mixing ratios at EPA monitoring sites in Georgia, Alabama, and Mississippi exhibited statistically-significant ( $p < 0.0001$ ) linear correlations with annual NO<sub>x</sub> emissions in those states, decreased by ~30% on average, and declined at rates averaging ~1 ppbv y<sup>-1</sup>. Ozone production efficiency (OPE, molecules of O<sub>3</sub> produced per molecule of NO<sub>x</sub> oxidized) increased by factors of ~2 or more between 1999 and 2014, which partially offset the ~60% NO<sub>x</sub> emission reductions and limited the O<sub>3</sub> decreases. The results suggest increasing responsiveness of O<sub>3</sub> to NO<sub>x</sub> as NO<sub>x</sub> emissions decline, but the effectiveness of ongoing NO<sub>x</sub> emission reductions will depend on the balance between changes in observed OPE and ambient NO<sub>x</sub> 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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