Summary of revisions

Review 1

For convenience, the text of the reviewer is reproduced here in red, interspersed with our responses.

First, if not all of the NOz is measured, that will lead to a high bias.

We expanded the discussion of measurement accuracy to include the following. The SEARCH measurements of NO_y were designed to capture particulate nitrate and organic nitrates, as well as NO, NO_2, HNO_3, and other oxidized nitrogen species. The NO_y sampler derives from the ESE instrument discussed in Williams et al. (1998), which was one of five instruments for which measurements of NO_y reproduced the sum of separately measured NO_y species. Additional testing in 2013 showed that SEARCH NO_y measurements agreed with the sum of measured mixing ratios of NO, NO_2, HNO_3, 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 NO_2 is NO_2-specific, but over time the instruments utilized three different types of lamps for the photolytic conversion of NO_2 to NO. We therefore tested for biases in the O_3-NO_z relationships by determining O_3-HNO_3 relationships, and concluded that similar temporal changes occurred in both sets of relationships.

Second, they present their method for trying to make sure that the background ozone is not biasing the calculation. While I appreciate the effort, they really don't show that it works. (They do an analysis, but in the end, it is not very satisfying and needs a bit more analysis and justification.)

Since that supplemental analysis is limited by the available data, we expanded the discussion to cover supporting information from other studies to include the following. O_3 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 O_3 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 O_3 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 O_3 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_3 versus NO_z. Moreover, the actual O_3 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_3, have previously been used as indicators of changes in regional or continental background O_3 (e.g., Wilson et al., 2012). The 5th percentile peak daily 8-hour O_3 mixing ratios decreased during summer at rural sites throughout the southeastern U.S. between 1988 and 2014 (Lin et al., 2017). By this measure, background O_3 levels were not increasing in the southeastern U.S. during our study period and therefore could not have introduced a positive bias in observed slopes of summer O_3 versus NO_z.

The trend in the 95th percentile summer peak daily 8-hour O_3 mixing ratios in the southeastern US reported by Lin et al. is ~ -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 O_3 mixing ratios occurring each month) declined at all SEARCH sites at statistically significant ($p < 0.01$) rates averaging ~1 ppbv yr^{-1} (our Figure 3).

Anthropogenic emissions and long-range transport (long-range tropospheric + stratospheric) O_3 each accounted for about 40% (15 – 20 ppbv) of model-predicted O_3 below 1 km altitude at Huntsville, AL, during June 2013, while long-range transport accounted for ~80% of model-predicted O_3 above 4 km altitude (Johnson et al., 2016). Using ozonesondes that are launched on a typically weekly schedule, vertical O_3 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 O_3 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_3, 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 O_3-NO_z relationships are not biased by trends in transport of background O_3.

The comparison of their OPE's to modeled values is of interest, but again, unsatisfying. Do the Liu et al., values of up to 80 make sense? Do OPEs of 20 for a NOx of 1 ppb make sense given their results? It would be good if they provide some critical analysis. If the OPEs increased from their values of, currently, about 20, to 80, while the NOz decreases from 1 to 0.1 ppb. Wouldn't this lead to ozone levels below background and well below their asymptotic values? Please comment. When they say that for a limit of OPE approaching zero: : : Why does one presuppose such a limit? That is in contrast to Liu et al.

We revised this discussion. We added discussion of Reynolds et al. (2004), which is the modeling analysis that is most relevant to our study. We also clarified the applicability (or non-applicability) of related studies. We eliminated the references to OPE that are inapplicable.

It is not apparent they are capturing all of the oxidized N in their work. How much of the organic N is measured (e.g., the fraction with the PM)? When they are using NOz, are they missing much (how much)? We expanded the discussion of measurement accuracy, as noted above.

Discussion of VOC reactivity: OH reactivity is a poorly used measure of ozone formation from VOCs. USE MIR or MOIR ([Carter, 1994])

We eliminated panel (d) of Figure 6, and simply referenced the literature on isoprene reactivity and the significance of seasonal isoprene emissions in the Southeast. 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.

Figure 2: What is the -10th %ile? Do you mean 10th %ile? (No minus)

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

The Abstract is currently not very informative. More hard results should be provided. To say "O3 declines are less than proportional to the decreases in NOx" is obvious to most folks: : : there is a very non-zero ozone background, so you expect less than proportional. While they say OPE has increased, they don't say by how much. They don't say what are the ozone reductions. Provide some details. If I just read the abstract I would not have learned much, and would not really be included to read the article.

We revised the abstract (as well as the conclusions and a new section on implications) to provide details and explain the larger significance of the study.

The atmospheric chemistry primer (section 2.1) is too basic for the readers of ACPD. Some parts are fine but assume the readers know reactions R1-R7.

We deleted the equations. 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.

In summary, the paper is informative, though I believe a number of modifications and further analysis are required for acceptance.

We have provided a major revision.

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Review 2

We appreciate the reviewer's affirmation of the value of the SEARCH program and database. We have revised the manuscript as summarized following each of the reviewer's major and minor points. For convenience, the entire text of the reviewer is reproduced here in red, interspersed with our responses.

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 NOx 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 NOx oxidized) increased between 1999 and 2014, which affected the magnitude of the O3 response to NOx 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 NOx, but the effectiveness of ongoing NOx emission reductions will depend on the balance between changes in observed OPE and ambient NOx 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.

We revised the abstract to address points raised by both reviewers. The preceding three comments are discussed below (reviewer's point 1 under is addressed under point 4 and reviewer's point 2 under point 7). Regarding point 1, our results can simply be presented as rates over time with stated error limits (as we have done), without asserting that they are either proportional or non-proportional. Regarding reviewer's point 3, the last sentence of the abstract was intended as a caveat about the limitations of extrapolating past to future trends, rather than a conclusion, and has been rephrased.

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 NOx 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.

We added comparisons to other studies and discussed them.

Second, it would be more informative to compare the percentage declines in NOx 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 NOx 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 NOx (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.

We added intercept-corrected comparisons for the EPA AL-GA data in the discussions of Figure 2 and the SEARCH data in Table S2. We did not do this for other papers.

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.

It is better for us to present the full record and then add results that are restricted to the later years for comparison, since we cannot justify starting the trends at an arbitrary date. We added text to Figure 3 to describe the post-1999 trends. We also added reference to modeling by Reynolds et al. (2004), which provides context for the observed trends.

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 Ox (= 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 NOx to NOz through NO3 and N2O5 chemistry, which destroys rather than produces O3.

Figure 5 has been replaced.

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.

We rewrote Section 4.4. Section 4.4.1 is now restricted to presenting the basic regression results and demonstrating that these results exhibit temporal changes. Section 4.4.2 compares results to those reported elsewhere, discusses the relevance of the comparisons, and examines issues raised by the reviewer.

Specific difficulties include:

- Ozone is quite low (≤20 ppb) at low NOz 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 NOz 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-NOz relationships in the transported regional background, and provide little or no information regarding ozone formation within the SEARCH region.

The new discussion of transported O_3 in Section 4.1 indicates that transported O_3 mixing ratios are consistent with the intercepts shown in our figures. We revised Figure 9 to differentiate types of weather. We added discussion of the sensitivity of the results to variations in O_3 transport.

- Figure 9 gives linear fits of observed O3 vs NOz 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.

As we had noted near the end of Section 4.4.1, intercepts and slopes are expected to be related if determined for successive tangents to a non-linear relationship. Nonlinearity is indicated in Figure 8 and in new Figure S14. The downward trends in NO_z and HNO_3 mixing ratios means that older data represent tangents determined for higher mean NO_z and HNO_3 mixing ratios.

- The paragraph beginning on pg. 12, line 7 attempts to account for the influence of depositional loss of NOz 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.

We explained why the difference-based regressions are expected to yield different results and why the statistical uncertainties are high. Please see the caveat about the 2001 data that we expressed in Section 3.1 and in the captions of Figure 8 and Figure S3. Although we could remove selected years from the analysis, we prefer to retain them with the caveats.

- 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.

We agree that the definitions of background differ among studies. We clarified these differences and added the citation to Berlin et al. (2013).

- 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.

We revised this discussion. We expanded the discussion of modeling work by Reynolds et al. (2004), which is directly relevant to our study region and time period.

- 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

We added comments on this matter to the beginning of Section 4.4.2.

- 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.

Revised and retitled.

7) The Conclusions section must be revised consistent with the revisions needed to address the above issues.

Revised.

Minor issues:

1) Line 11: typo - "... in in Alabama and Georgia."

Corrected.

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 NOx 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.

Change made and text revised.

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 NOx 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.

We revised Figure S4 and added a statement about HNO_3 and NO_y trends to the text.

4) The de Gouw et al., 2014 reference is omitted from the References list.

Corrected – it was there, it had just run into the previous reference due to a missing line break.

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 his 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.

Revised.

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)."

Revised with different wording than suggested, because the statistical model was not based on linear correlations and it controlled for multiple meteorological factors.

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.

We added these citations as well as other references and placed an expanded discussion of background trends in the first section of the results.

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.

Because the discussion of reactivity references previous work, and because the other referee proposed using the MIR and MOIR reactivity scales in place of k_{OH} reactivity (which was what was previously published), we removed the statements about reactivity. The k_{OH} reactivity results could be reproduced here, but additional computations of MIR and MOIR reactivity are beyond the scope and focus of the present manuscript. The seasonal variations of isoprene mixing ratios are evident in Figure 6 and show its importance during summer.

References

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Ozone Response to Emission Reductions in the Southeastern United States

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Abstract. Ozone (O_3) formation in the southeastern U.S. is studied in relation to nitrogen oxide (NO_x) emissions using long-term (1990s – 2015) surface measurements of the Southeastern Aerosol Research and Characterization (SEARCH) network, U.S. Environmental Protection Agency (EPA) O_3 measurements, and EPA Clean Air Status and Trends Network (CASTNet) nitrate deposition data. Annual 4th-highest daily peak 8-hour O_3 mixing ratios at EPA monitoring sites in Georgia, Alabama, and Mississippi exhibit statistically-significant ($p < 0.0001$) linear correlations with annual NO_x emissions in those states between 1996 and 2015. The annual 4th-highest daily peak 8-hour O_3 mixing ratios declined toward values of ~45 – 50 ppbv and monthly O_3 maxima decreased at rates averaging ~1 – 1.5 ppbv y^{-1}. Mean annual total oxidized nitrogen (NO_y) mixing ratios at SEARCH sites declined in proportion to NO_x emission reductions. CASTNet data show declining wet and dry nitrate deposition since the late 1990s, with total (wet plus dry) nitrate deposition fluxes decreasing linearly in proportion to reductions of NO_x emissions by ~60% in ~~in~~ Alabama and Georgia. Annual nitrate deposition rates at Georgia and Alabama CastNet sites correspond to 30% of Georgia emission rates and 36% of Alabama emission rates, respectively. The fraction of NO_x emissions lost to deposition has not changed ~~over time~~. SEARCH and ~~EPA~~ CASTNet sites exhibit ~~comparable~~ downward trends in mean annual nitric acid (HNO_3) concentrations. ~~Mean annual total oxidized nitrogen (NO_y) mixing ratios at SEARCH sites declined in proportion to NO_x emission reductions. Annual 4th-highest daily peak 8-hour O_3 mixing ratios at EPA monitoring sites in Georgia, Alabama, and Mississippi exhibit statistically-significant ($p < 0.0001$) linear correlations with annual NO_x emissions in those states between 1996 and 2015. The annual 4th-highest daily peak 8-hour O_3 mixing ratios are declining toward non-zero values of ~45 – 50 ppbv. The O_3 declines are less than proportional to the decreases in NO_x emissions: emissions decreased by ~60% and O_3 maxima declined ~30 – 35% at rates averaging ~1 ppbv y^{-1}. Ozone production efficiency (OPE, molecules of O_3 produced per molecule of NO_x oxidized) increased between 1999 and 2014, which affected the magnitude of the O_3 response to NO_x emission reductions by partially offsetting precursor decreases and contributing to the nonlinear O_3 response.~~ Observed relationships of O_3 to NO_z (NO_y – NO_x) ~~The results~~ support past model predictions of increases in cycling of NO and~~suggest~~ increasing responsiveness of O_3 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).~~ The study data provide a long-term record that can be used to examine the accuracy of process relationships embedded in modeling efforts. Quantifying observed O_3 trends and relating them to reductions in ambient NO_y species

concentrations offers key insights into processes of general relevance to air quality management and provides important information supporting strategies for reducing O_3 mixing ratios.

1 Introduction

Ozone (O_3) is a well-known and important product of photochemical processes in the troposphere involving nitric oxide (NO), nitrogen dioxide (NO_2), and volatile organic compounds (VOCs). Ozone is of broad interest for its adverse effects on humans and ecosystems, as reflected by regulation through the U.S. Clean Air Act (e.g., U.S. EPA, 2014; 2015a).

Regulatory actions address extreme O_3 mixing ratios: the U.S. National Ambient Air Quality Standard (NAAQS), currently 70 ppbv, is applicable to the annual 4th-highest daily eight-hour maxima averaged over three--year periods (U.S. EPA, 2015b; 2015c). By the early 1990s, U.S. emission control efforts began to focus on nitrogen oxides ($NO_x = NO + NO_2$) in addition to VOCs (NRC, 1991). O_3 management has generally relied on precursor reduction requirements estimated from models that integrate descriptions of non-linear chemical and atmospheric processes (e.g., Seigneur and Dennis, 2011), and guidance has also derived from so-called "observation-based" models linking O_3 and its precursors based on chemical reactions that are believed to drive ambient mixing ratios (e.g., NARSTO, 2000; Schere and Hidy, 2000).

Most of the work developing an observational basis for O_3-precursor chemistry derives from field campaigns, sometimes focusing on urban conditions. Short-term data are available from aircraft flights, for example, or summer field measurements made at a variety of locations. Such studies usually are limited to a month or two of intense sampling. One example in the southern U.S. is the 1990 ROSE Experiment at Kinterbish, a rural, forested state park in western Alabama (Frost et al., 1998). This summer study of rural O_3 at low anthropogenic VOC and low NO_x mixing ratios provided important insights into rural O_3 formation (Trainer et al., 2000). Other examples of short-term campaigns across the U.S. and elsewhere are reviewed in Solomon et al. (2000). More recent field studies include New England in 2002 (e.g., Griffin et al., 2004; Kleinman et al., 2007), Texas in 2006 (e.g., Berkowitz et al., 2005; Neuman et al., 2009), the mid-Atlantic region in 2011 (He et al., 2013), California in 2010 (Ryerson et al., 2013), Colorado in 2012 and 2014 (e.g., McDuffie et al., 2016), and the southeastern U.S. in 2013 (e.g., Neuman et al., 2016; Warneke et al., 2016). These campaigns and accompanying analyses of O_3 production and accumulation typically address summer, which historically has the strongest photochemical activity. However, strong photochemical O_3 production can occur under special circumstances in winter (e.g., Schnell et al., 2009).

Accounting for an O_3 background is important. O_3 background is associated with biogenic influence, large-scale transport, or the potential influence of the upper atmosphere (e.g., stratospheric intrusions, especially during spring) (e.g., Lin et al., 2012; Langford et al., 2015). The nature and magnitude of background O_3 remain an active area of research in the U.S. and Europe (Naja et al., 2003; Solberg et al., 2005; Ordóñez et al., 2007; Cristofanelli and Bonasoni, 2009; Arif and Abdullah, 2011; Zhang et al., 2011; Wilson et al., 2012). Hidy and Blanchard (2015) discuss definitions of continental and regional background O_3. For this study, we adopt a definition of "background" that includes both the non-anthropogenic component and the southeastern regional component (Section 4.4.1).

Field studies have provided observational evidence of non-linearity in O_3-NO_z relationships (e.g., Trainer et al., 1993; Kleinman et al., 1994; Trainer et al., 1995; Hirsch et al., 1996; Frost et al., 1998; Kasibhatla et al., 1998; Nunnermacker et al., 1998; St. John et al., 1998; Sillman et al., 1998; Zaveri et al., 2003; Griffin et al., 2004; Travis et al., 2016). Long-term, post-1990s data are widely available for O_3 and NO_2 but detailed observations of total oxidized nitrogen (NO_y) and VOC, and especially their component species, are typically lacking (e.g., Hidy and Blanchard, 2015). One of the longest records of urban and suburban data, comprising a series of short-term campaigns as well as continuous measurements, is from southern California. This region exemplifies a photochemically active urban regime. An analysis of multi-decadal (since the 1960s) data by Pollack et al. (2013) reveals how changes in atmospheric chemical reactions have contributed to the observed reductions of O_3 in southern California since 1973. Long-term (more than one decade) measurements characterizing O_3 and NO_y relationships in both urban and rural conditions are less common.

The photochemical regime in the Southeast represents humid subtropical conditions with urban emissions yielding elevated O_3 levels superimposed on a general regional background (Chameides and Cowling, 1995). The EPA O_3 and deposition data provide a regional basis for characterizing trends since the early 1980s (U.S. EPA 2016a; 2016b). In addition, the Southeastern Aerosol Research and Characterization (SEARCH) project (Hansen et al., 2003; Hidy et al., 2014) provides measurements that can be used to investigate changes in O_3 production resulting from changes in anthropogenic emissions in the southeastern U.S. The SEARCH network of eight sites began with the Southeastern Oxidant Study (SOS) (Chameides and Cowling, 1995; Meagher et al., 1998) rural locations, which were near (1) Centreville, AL, ~85 km southwest of Birmingham, (2) at Yorkville, GA, ~60 km northwest of Atlanta, GA and (3) at Oak Grove, MS, ~40 km southeast of Hattiesburg, MS, and 75 km north of Gulfport, MS, on private land within the confines of the Desoto National Forest (Hansen et al., 2003). Measurements of some gas-phase species began at these rural sites in 1992, thus providing a rural data record of over 20 years. Beginning in 1999, SEARCH added five sites in metropolitan Atlanta, GA, Birmingham, AL, Pensacola, FL, and Gulfport, MS.

Our goal for this study is to extend earlier analyses of the photochemical response of O_3 to precursors through 2014, emphasizing relationships between O_3 and NO_y. We first summarize relevant O_3 photochemistry to provide a context for the observational analysis. We then describe trends in emissions and ambient pollutant concentrations, and discuss O_3, NO_z, and HNO_3 observations at the SEARCH sites. The trends in O_3 mixing ratio, NO_x precursor emissions, and ambient nitrogen oxide mixing ratios offer important insight into future changes in O_3 and NO_y. Blanchard et al. (2014) previously explained the majority (66 - 80%) of the day-to-day variations in daily peak 8-hour average O_3 at SEARCH sites during March – October of 2002 - 2011 using meteorological variables coupled with ambient measurements of O_3 precursors (NO, NO_2; limited measurements of VOCs) and NO_x photochemical reaction products (NO_z) and a statistical model ~~(Blanchard et al., 2014)~~. The previous analyses are extended here for data through 2014 to ~~determine observed O_3 production efficiency (OPE). The analysis explains~~help understand ongoing and potential future O_3 changes in relation to changes in ambient NO_z and HNO_3 mixing ratios in the southeastern U.S. Results are discussed in relation to modeling predictions by Reynolds et al. (2004) and others.

2 Ozone-Nitrogen Oxide Chemistry

2.1 Key Atmospheric Reactions Linking O_3 with NO_x

Net tropospheric O_3 accumulation occurs when sunlight acts on VOC and NO_x emissions and the O_3 production rate exceeds O_3 loss (Trainer et al., 2000). Tropospheric O_3 mixing ratios are affected by solar intensity, chemical formation and loss (e.g., deposition) rates of O_3, the rate of dispersion of O_3 and its precursors, meteorological factors, vertical entrainment and transport of plumes. NO_2 forms rapidly by reaction of NO with O_3 and photolysis of NO_2 produces O_3, yielding steady-state mixing ratios of NO, NO_2, and O_3 in the absence of other species as expressed by the photostationary state, or Leighton relationship (Seinfeld, 1986). ~~The key reactions are (Seinfeld, 1986):~~

~~(R1) NO + O_3 => NO_2 + O_2~~

~~(R2) NO_2 + $h\nu$ => NO + O~~

~~(R3) O + O_2 => O_3~~

In the troposphere, NO_2 also forms by reaction of NO with peroxy (HO_2) and alkyl peroxy (RO_2) free radical species, which derive in turn from the reaction of VOCs with hydroxyl (HO), HO_2, RO_2, and alkyl radicals (Seinfeld, 1986). Radical production from VOCs creates a pathway for conversion of NO to NO_2 that does not consume O_3 (Atkinson, 2000), which then leads to higher O_3 mixing ratios. ~~Key reactions are (Seinfeld, 1986):~~

~~(R4) RH + $HO^{\bullet}$ => $R^{\bullet}$ + H_2O~~

~~(R5) $R^{\bullet}$ + O_2 => $RO_2^{\bullet}$~~

~~(R6) $RO_2^{\bullet}$ + NO => $RO^{\bullet}$ + NO_2~~

~~(R7) $HO_2^{\bullet}$ + NO => $HO^{\bullet}$ + NO_2~~

~~(R8) $HO^{\bullet}$ + NO_2 => HNO_3~~

O_3 accumulation is typically associated with high solar radiation intensity and temperatures favoring atmospheric reactions, lower wind speeds, and high anthropogenic emission rates (NARSTO, 2000). O_3 accumulation requires NO mixing ratios exceeding approximately 10 to 30 pptv (Atkinson, 2000; Logan, 1985), along with the presence of HO_2 and RO_2 radicals that react with NO to form NO_2. The former conditions are normally met in urban air; NO_x mixing ratios are much lower under typical conditions in rural southeastern areas, but still well above 30 pptv ~~as reported in the U.S.~~ (e.g., Hudman et al., 2007; Travis et al., 2016). Under these conditions, the O_3 photochemical production rate is proportional to the ambient NO multiplied by the sum of HO_2 and RO_2 radical mixing ratios, where the latter are weighted by their rates of reaction with NO (Trainer et al., 2000). Field studies show that observed rates of rural O_3 production are proportional to the rate of oxidation of NO_x. Where VOCs are present for radical production and NO_x is rate-limiting (Trainer et al., 2000), regional O_3 production can be expressed in terms of the derivative $d[O_3]/d[NO_x]$, denoted the O_3 production efficiency (OPE) (Liu et al.,1987). OPE is understood as the number of molecules of O_3 formed per molecule of NO_x oxidized and OPE increases as NO_x mixing ratios decrease (Liu et al., 1987; Trainer et al., 2000). OPE reflects the mean number of NO-NO_2 cycles occurring, in which each photolysis of one NO_2 molecule generates one O_3 molecule until that NO_2 molecule is oxidized to nitric acid (HNO_3) or to other species such as peroxyacetylnitrate (PAN). NO_x reaction products, including HNO_3 and PAN, comprise NO_z. For chemical reactions, the quantity $d[O_3]/d[NO_z]$ is equivalent to $d[O_3]/d[NO_x]$ but with opposite sign, and has therefore been used to estimate OPE; limitations due to confounding influences of emissions, transport, and deposition are discussed in Sections 4.3 and 4.4.

Empirically, the slope of a linear fit of afternoon O_3 (or $O_x = O_3 + NO_2$) versus NO_z has been used to estimate OPE (e.g., Trainer et al., 1993; Pollack et al., 2013). This estimate is subject to certain limitations because it does not explicitly account for: (1) day-to-day variability in "old" (baseline or regional background) O_3 mixing ratios, (2) mixing of air masses having different emission histories, (3) rapid loss of HNO_3 (primarily through dry deposition, but also through gas-to-particle conversion) (Trainer et al., 2000), and (4) regeneration of NO_2 from PAN and certain other species. Because PAN regenerates NO_2, it can serve as a reservoir rather than a true NO_2 sink (Singh and Hanst, 1981; Singh, 1987). In contrast, HNO_3 largely terminates the cycling between NO and NO_2. Therefore, the relative yields of PAN and HNO_3 are of importance. Despite such limitations in using measurements to quantify OPE, data from field studies have been used since the 1990s to determine upper bounds for OPE and the results have continued to appear in the literature as an indicator of relevance to O_3 chemistry (e.g., Berkowitz et al., 2005; Neuman et al., 2009; Kim et al., 2016). Investigators caution that field measurements reveal the net of production and loss, which potentially overestimates actual OPE by factors of 3 to 6 due to rapid chemical and deposition losses of HNO_3 and other NO_z species (e.g., Trainer et al., 2000). Additional discussion ~~of this ambiguity~~ is found in Section 4.4.

~~Factors other than OPE are relevant to characterizing O_3 production and accumulation. In one case, OPE has not changed over time i~~In southern California, ~~but~~ changes in the relative proportions of NO_x-oxidation products have occurred and are thought to be instrumental in driving the rapid rates of O_3 decline in that area (Pollack et al., 2013). These results indicate that measurements of HNO_3 or PAN are needed to identify important changes in chemical pathways~~, considering not only OPE as defined by afternoon O_3/NO_z but also by using other indicators of O_3 production or accumulation, such as the O_3/HNO_3 ratio~~.

2.2 National O_3 Response to Emission Reductions

Between 1980 and 2013, the national average of the annual 4th-highest peak daily 8-hour O_3 mixing ratios, a metric relevant to the U.S. O_3 NAAQS, declined by 33% (U.S. EPA, 2015d) as national VOC and NO_x emissions decreased by 53% and 52%, respectively (U.S. EPA, 2015e). Across the U.S. and on multiple spatial scales from continental to urban, annual 4th -highest daily peak 8-hour O_3 mixing ratios between 1980 and 2013 show a statistically significant ($p < 0.05$) linear fit to either annual average or to 98th percentile daily maximum hourly NO_2 mixing ratios; regression slopes are less than 1:1 and intercepts are in the range of 30 to 50 ppbv O_3 (Hidy and Blanchard, 2015). Proportionalities between O_3 and NO_2 that are less than 1:1 are expected, and the observed intercept terms are approximately consistent with typical O_3 mixing ratios of ~20 – 50 ppbv observed at remote monitoring sites (Oltmans et al., 2008; 2013; U.S. EPA, 2012; Fiore et al., 2014; Lefohn et al., 2010; 2014; Cooper et al., 2012; 2014).

Although nonlinearity of O_3 production and accumulation with respect to ambient VOC and NO_x is well established (Lin et al., 1988), a tendency toward linearity is expected at sufficiently low NO_x mixing ratios. As an example, the O_3 photochemical production rate during June 1990 at Kinterbish, AL was approximately linear over a range of ambient NO_x from 0.1 to 2 ppbv (Trainer et al., 2000). Observed O_3 extrema can also exhibit an apparent linear or near-linear response to ambient NO_x mixing ratios if the extrema consistently fall within the lower-right quadrant (NO_x-sensitive regime) of an O_3-VOC-NO_x diagram, a concise graphical representation first established empirically from southern California data and later generated using the Empirical Kinetics Modeling Approach (EKMA) (illustrated in Hidy and Blanchard, 2015). The -O_3-VOC-NO_x diagram has been adopted by many investigators for displaying the output of box models (e.g., Fujita et al., 2003; 2015) and grid-based photochemical models (e.g., Reynolds et al., 2003; 2004).

Southern California historically has exhibited the highest peak O_3 mixing ratios in the U.S. since the 1960s. Because of high ambient O_3 and precursor mixing ratios there and the complexity of the relationships of O_3 with NO_x and VOC, some investigators have described southern California O_3 and precursor trends in terms of percentage changes. For example, Pollack et al. (2013) report that peak 8-hour O_3 mixing ratios in southern California declined exponentially over time at a rate of 2.8% per year between 1973 and 2010, thus decreasing O_3 levels by approximately a factor of three. This rate of O_3 decline exceeds rates occurring in other metropolitan areas (Hidy and Blanchard, 2015). O_3 extrema in southern California decreased along with declining mixing ratios of ambient VOCs and NO_x (7.3% yr^{-1} and 2.6% yr^{-1}, respectively, 1960 – 2010) and declining ratios of VOC/NO_x (4.8% yr^{-1}) (Pollack et al., 2013). The rates of atmospheric oxidation of NO_x increased over time and changes in NO_x oxidation reactions increasingly favored production of HNO_3, a NO_x reaction product associated with radical termination and quenching of the O_3 formation cycle (Pollack et al. 2013). To our knowledge, changes in the relative proportions of atmospheric reaction products accounting for rapid rates of O_3 reduction have not been reported for locations other than southern California.

3 Methods

3.1 Emissions and Ambient Air Quality Measurements

Air quality monitoring data were obtained from the EPA Air Quality System (AQS) data archives for all sites in Georgia, Alabama, and Mississippi (U.S. EPA, 2016a). Daily measurement values (i.e., peak daily 8-hour O_3 mixing ratio) as well as annual summary statistics (e.g., maxima, annual averages) were acquired. We obtained deposition data from the two EPA Clean Air Status and Trends Network (CASTNet) monitoring sites located within the study region: Sand Mountain, AL (125 km ENE of the SEARCH site at Centreville) and Georgia Station, GA (102 km SE of the SEARCH site at Yorkville) (U.S. EPA, 2016b).

Annual, state-level emission trends data were obtained from U.S. EPA (2016c; 2016d), Xing et al. (2013), and Hidy et al. (2014). Comparability of inventories is discussed in the supplementary material (Figure S1). Because the EPA trend inventory utilized different methods for estimating mobile source emissions prior to 2002 compared with 2002 and later years, we combined EPA trend estimates for 2002 – 2016 with the 1996 - 2001 emission estimates of Hidy et al. (2014), which are consistent with more recent EPA methods (supplementary material).

Hourly measurements of gases (NO, NO_2, NO_y, HNO_3, and O_3) were obtained from SEARCH public archives (Atmospheric Research and Analysis [ARA], 2017). All parameters measured at the sites are calibrated and audited to conventional reference standards, as described in ARA (2015). Network operations, sampling, and measurement methods are documented in Hansen et al. (2003; 2006); see also Table S1. The network consisted of eight extensively instrumented monitoring sites located in the southeastern U.S. along the Gulf of Mexico and inland (Figure S2): Pensacola, Florida (PNS) and Gulfport, Mississippi (GFP), urban coastal sites (~ 5 km and 1.5 km from the shoreline, respectively); Pensacola – outlying (aircraft) landing field (OLF) and Oak Grove, Mississippi (OAK), non-urban coastal sites near the Gulf (~20 km and 80 km inland, respectively); Atlanta, Georgia – Jefferson Street (JST) and North Birmingham, Alabama (BHM), urban inland sites; and Yorkville, Georgia (YRK) and Centreville, Alabama (CTR), non-urban inland sites. PNS, OAK, and GFP were closed at the end of 2009, 2010, and 2012, respectively. SEARCH site locations are described in detail, including discussion of possible emission influences, in Hansen et al. (2003) and Hidy et al. (2014). SEARCH VOC data are available for JST as daily data from 1999 through 2008, and U.S. EPA VOC measurements are available for YRK as summer hourly data and as 24-hour samples collected every sixth day throughout the year (Blanchard et al., 2010). EPA VOC samples are also available for three other sites in the Atlanta area; only one of these additional sites reported data through 2014.

SEARCH meteorological parameters and gases are sampled at a height of 10 meters, characteristic of lower troposphere mixing ratios near the surface (Hansen et al., 2003; Hansen et al., 2006; Edgerton et al., 2007; Saylor et al., 2010). Gas and meteorological measurements commenced in 1992 at the rural sites of CTR, OAK, and YRK. The measurements at rural SEARCH sites included O_3, NO, and NO_y beginning in 1992, and NO_2 and HNO_3 measurements began in 1996. Consistent measurement methods have been utilized for all gases except NO_2. NO_2 measurements commenced network-wide in 2002, and three NO_2 measurement methods have been employed during the network operations (Table S3). All three methods are NO_2-specific, differing primarily in the light source used for photolysis of NO_2. The NO_2 data exhibit consistency with NO and NO_y measurements but with some variations occurring during specific years (e.g., 2001 and 2002, Figure S3). Because changes in NO_2 measurement methods could affect the computed NO_z (NO_y – NO – NO_2), we repeat some data analyses using HNO_3 in place of NO_z. As noted, HNO_3 data also provide useful insight into NO_2 termination reactions. HNO_3 measurements are the difference between NO_y and denuded NO_y (Table S1; Hansen et al., 2006). The SEARCH measurements of NO_y were designed to capture particulate nitrate and organic nitrates, as well as NO, NO_2, HNO_3, and other oxidized nitrogen species. The NO_y sampler derives from the instrument identified in Williams et al. (1998) as "ESE", which was one of five instruments for which measurements of NO_y reproduced the sum of separately measured NO_y species. Additional testing in 2013 showed that SEARCH NO_y measurements agreed with the sum of measured mixing ratios of NO, NO_2, HNO_3, particulate nitrate, alkyl nitrates, and peroxy–alkyl nitrates (Hidy et al., 2014).

Trace gas calibrations we~~a~~re done daily for O_3 and every third day for other gases. Reported detection limits (Table S1) are 0.05 – 0.1 ppbv for oxidized nitrogen species and 1 ppbv for O_3 (Hansen et al., 2003; 2006). NO_2 measurement uncertainties are estimated as ~30% prior to 2002 and ~10% after 2002 (Hansen et al., 2006). Measurement uncertainties are estimated to be 10% or less for other oxidized nitrogen species and 5% or less for ozone (2 sigma in all cases). Propagation of errors indicates corresponding 2-sigma measurement uncertainties averaging 0.5 ppbv for mid-afternoon NO_z (< 0.1 ppbv for NO_z < 1 ppbv) and 0.16 for the ratio NO_z/NO_y.

3.2 Data Analysis

Multiple methods were employed to characterize the variability of ambient O_3 and NO_y mixing ratios. Analyses of seasonal variability used data from all months of each year. Diurnal hourly average mixing ratios were computed by year to characterize patterns of temporal change and to identify hours associated with O_3 maxima. Observed ~~OPE~~ slopes of regressions of O_3 versus NO_z were~~as~~ computed as previously done in measurement studies using afternoon O_3 and NO_z data (Trainer et al., 1993; Kleinman et al., 1994; Trainer et al., 1995; Hirsch et al., 1996; Kasibhatla et al., 1998; Nunnermacker et al., 1998; St. John et al., 1998; Sillman et al., 1998; Zaveri et al., 2003; Griffin et al., 2004; Travis et al., 2016). Because past studies have examined O_3 formation in photochemically aged air (i.e., at locations distant from fresh emissions, where atmospheric reactions have acted on emissions from earlier times) during summers (e.g., Trainer et al., 1993), ~~the~~ our analyses ~~of summer OPE~~ focus on the months of June and July to select weeks nearest maximum solar radiation (~ -20 days, + 40 days). Additional analyses ~~of OPE~~ were carried out for other months to facilitate comparisons across seasons. As for earlier studies, the calculations are based on afternoon times, using hourly values starting at 2 p.m. local standard time to represent the daily peak O_3 after morning production and before mixing ratios decline with decreasing photochemical reaction in later afternoon. In addition to characterizing O_3/NO_z and its change with time, corresponding supporting analyses are presented for O_3/HNO_3. As a supplemental analysis, rates of maximum diurnal increase of O_3 and HNO_3 during late morning and early afternoon were computed for comparison of ΔO_3 with ΔHNO_3.

4 Results and Discussion

4.1 Trends

Hidy et al. (2014) report a 63% reduction of NO_x emissions in the southeastern U.S. between 1996 and 2014. The largest NO_x emission changes in the Southeast occurred between 2007 and 2009 due to reductions of emissions from electric generating units (EGUs) and from diesel engine vehicles, and were accompanied by more gradual year-to-year reductions of gasoline-engine mobile-source NO_x emissions (de Gouw et al., 2014; Hidy et al., 2014). NO_x emission reductions led to approximately proportional responses of mean ambient NO_y and NO_z mixing ratios at SEARCH sites (Hidy et al., 2014).

The EPA CASTNet data show ~~declining~~ wet and dry nitrate deposition since the late 1990s declining at rates of ~5% per year (-0.045 ± 0.005 and -0.056 ± 0.005 y^{-1}), nearly identical to NO_x emission changes of -0.046 ± 0.001 and -0.051 ± 0.003 y^{-1} (Figure 1). ~~with~~ T~~t~~otal (wet plus dry) nitrate deposition fluxes decreased~~ing~~ linearly in proportion to reductions of NO_x emissions in ~~in~~ Alabama and Georgia (Figure 1). Linear regression slopes indicate that the annual nitrate deposition fluxes at the Georgia and Alabama CASTNet sites correspond to 30% of Georgia emissions and 36% of Alabama emissions on an annual and statewide basis (Figure 1). Emissions are not spatially homogeneous and deposition losses likely vary with distance from emission sources. The two sites are situated differently in relation to metropolitan areas, possibly affecting deposition fluxes; Sand Mountain (SND) is northeast of Birmingham and Georgia Station (GAS) is south of Atlanta. The linearity and statistical significance of the regressions indicates that the fraction of NO_x emissions lost to deposition has not changed over time (ratios of annual deposition-to-state-emissions varied without trend from 0.23 – 0.34 at GAS and 0.30 – 0.45 at SND). Mean annual SEARCH NO_y mixing ratios at rural CTR and YRK declined at ~5 – 7% y^{-1} (Figure S4). SEARCH and EPA CASTNet ~~and~~ sites exhibit ~~comparable~~ downward trends in mean annual HNO_3 concentrations of ~9 – 11% y^{-1} and ~6 – 7% y^{-1}, respectively (Figure S4). Ambient NO_y and HNO_3 trends are not statistically different from state-level NO_x emission trends.

Annual 4th-highest daily peak 8-hour O_3 mixing ratios at compliance monitoring sites in Georgia, Alabama, and Mississippi exhibit statistically-significant ($p < 0.0001$) linear correlations with annual NO_x emissions in those states between 1996 and 2015 (Figure 2), qualitatively consistent with past work indicating that high O_3 would respond to reductions of NO_x emissions (Chameides and Cowling, 1995; Jacob et al., 1995; Kasibhatla et al., 1998). ~~Spatial variability of~~Intersite differences in the annual 4th-highest daily peak 8-hour O_3 mixing ratios have~~s~~ decreased (Figure 2), consistent with an analysis of data from a larger number of U.S. and European locations (Paoletti, et al., 2014). The annual 4th-highest daily peak 8-hour O_3 mixing ratios are declining toward non-zero values, as indicated by the statistically-significant ($p < 0.0001$) intercepts of ~45 – 50 ppbv (Figure 2). ~~The O_3 declines are less than proportional to the decreases in NO_x emissions, as indicated by the ~60% emission reduction and ~30 – 35% O_3 declines shown in Figure 2, about equivalent to the national trends discussed in Section 2.2.~~~~multiple studies have demonstrated increasing trends in global background O_3 mixing ratios (Ordóñez et al., 2007; Oltmans et al., 2008; Arif and Abdullah, 2011; Wilson et al., 2012).~~

SEARCH data are used to characterize the southeastern O_3 response to emission changes in greater detail. Between 1999 and 2014, the highest peak daily 8-hour O_3 mixing ratios occurring each month (monthly O_3 maxima) declined at all SEARCH sites at statistically significant ($p < 0.01$) rates averaging ~1 – 1.5 ppbv y^{-1} (Figure 3). These declines are comparable to the trend in the 95th percentile summer peak daily 8-hour O_3 mixing ratios in the southeastern U.S. of ~ -0.8 to -1.8 ppbv yr^{-1} reported by Lin et al. (2017), with downward trends occurring in other seasons as well. ~~These trends are compared with emission changes in the Southeast, and with emission and O_3 trends in southern California, in Table S2.~~ The observed SEARCH O_3 trends are also consistent with other analyses of North American observations (e.g., Chan, 2009; Lefohn et al., 2010; Paoletti, 2014; Simon et al., 2015) and with the trends occurring at EPA monitors in the Southeast (Figure 2). Both EPA (Figure 2) and SEARCH (Figure 3) data suggest that O_3 mixing ratios increased during the 1990s, then began declining. This result is consistent with modeling by Reynolds et al. (2004), which predicted an initially slow response of Atlanta-area O_3 to emission reductions between 1996 and 2000, followed by increasing sensitivity to reductions of NO_x emissions. The observed O_3 decreases exceed those predicted by Reynolds et al. (2004) because actual NO_x emission reductions (~60% between 1996 and 2014) exceeded the projected emission reductions (~40% by 2010 and ~55% by 2020) that were anticipated based on known and anticipated emission control rules at the time of the modeling study. The~~se~~ SEARCH trends are compared with emission changes in the Southeast, and with emission and O_3 trends in southern California, in Table S2.

More complete understanding of regional O_3 trends requires consideration of both regional emission changes and possible changes in background O_3. Multiple definitions of the term “background O_3” may be found in the literature, including global background, continental background, non-anthropogenic background, and regional background, among others. For the O_3 trends shown in Figures 2 and 3, the most relevant consideration is the amount of O_3 transported into the study domain across upwind boundaries (denoted here as regional background or transported O_3). The percentage reductions of O_3 are larger if transported O_3 can be estimated and subtracted from observed O_3 mixing ratios, and this adjustment potentially provides a better assessment of the effects of regional emission reductions on the fraction of O_3 that is manageable by means of local and regional emission control measures. For example, Parrish et al. (2017a) report that the O_3 enhancement above background in Southern California decreased by 4.5% yr^{-1}, which is larger than the unadjusted O_3 decline of 2.8% y^{-1} given by Pollack et al. (2013). ~~Specific aspects of the observed O_3 trends are discussed in Sections 4.2 through 4.4.~~ Similarly, rates of decline in southeastern U.S. O_3 are larger if regional background O_3 is considered (Table S2).

Defining and estimating regional background (or transported) O_3 are each challenging. We interpret the intercepts in Figure 2 as indicators of mean O_3 levels that would occur on days with weather conducive to high O_3 in the absence of NO_x emissions from AL and GA sources, i.e., as estimators of O_3 transported into the region from outside the study domain (as discussed subsequently, multi-day carryover of local and regional emissions during stagnation events could also affect intercepts and slopes). Days with weather that is not conducive to high O_3 likely have different levels of transported O_3. The statistically-significant slopes in Figure 2 indicate O_3 enhancements that are attributable to AL-GA emissions, except as noted next, and a comparison of the O_3 decline to intercept-corrected O_3 would then reveal the proportionality between AL-GA emissions and AL-GA O_3 enhancements over O_3 originating outside the study domain (i.e., in excess of regional background O_3). Although the ~30 – 35% O_3 declines are less than proportional to the ~60% decrease in NO_x emissions, the decline in the median O_3 is ~60% if the 50 ppbv intercept shown in Figure 2 is subtracted from the O_3 mixing ratios.

If the amount of O_3 that has been transported from upwind regions has been changing over time, e.g., declining as NO_x emissions and ambient O_3 decline in adjacent regions, the slopes shown in Figure 2 would reflect changes in both the O_3 that originated upwind and in the O_3 enhancements attributable to AL-GA emissions, confounding attribution. Related studies do not provide consistent evidence for a trend, either upward or downward, in regional background O_3 in the southeastern U.S. For example, baseline O_3 concentrations in air flowing into Texas from the Gulf of Mexico during May through October did not change significantly between 1998 and 2012 (Berlin et al., 2013). Mean regional background O_3 mixing ratios were 48 ppbv to 59 ppbv in the Houston, TX, area on days with O_3 levels exceeding the NAAQS, which includes O_3 contributions from transport to the area from other regions of the U.S. (Berlin et al., 2013). Observed trends in the 5th percentile O_3 have previously been used as indicators of changes in either regional or continental background O_3 (e.g., Wilson et al., 2012). The 5th percentile peak daily 8-hour O_3 mixing ratios decreased during summer at rural sites throughout the southeastern U.S. between 1988 and 2014 (Lin et al., 2017). By this measure, regional background O_3 levels were not increasing in the southeastern U.S. during our study period.

Large-scale transport affecting O_3 in the boundary layer and at the surface is a function of altitude. For example, during June 2013, anthropogenic emissions and long-range transport (long-range tropospheric + stratospheric) O_3 each accounted for about 40% (15 – 20 ppbv each) of model-predicted O_3 below 1 km altitude at Huntsville, AL, while long-range transport accounted for ~80% of model-predicted O_3 above 4 km altitude (Johnson et al., 2016). This variation of source contributions with altitude provides an opportunity to differentiate between emission-related and transport-related trends derived from vertical soundings of upper-air O_3 mixing ratios. Using ozonesondes that are generally launched on a weekly schedule, vertical O_3 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 these ozonesonde data ($n = 940$ days) 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} ($p < 0.05$) in daily measurements at 0.5 km, -0.40 ± 0.10 ppbv y^{-1} ($p < 0.0001$) at 1 km (daily), -0.42 ± 0.09 ppbv y^{-1} ($p < 0.0001$) at 2 km (daily), and -0.57 ± 0.13 ppbv y^{-1} in monthly averages of O_3 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_3, no trends occurred: 0.06 ± 0.08 ppbv y^{-1} ($p > 0.1$) at 4 km (daily) and 0.09 ± 0.19 ppbv y^{-1} ($p > 0.1$) at 8 km (daily).

Global background is one component of regional background and trends in global background are expected to contribute to trends in regional background. Lin et al. (2017) show that rising NO_x emissions in Asia have increased modeled North American background O_3 levels (based on model simulations with zero North American emissions) by ~0.2 ppbv yr^{-1} in the southeastern U.S. in summer, which is a small effect even when cumulated over 20 years in comparison with the ~25 ppbv reduction in the median annual 4th-highest peak daily 8-hour O_3 shown in Figure 2. Multiple studies have demonstrated increasing trends in global background O_3 mixing ratios (Ordóñez et al., 2007; Oltmans et al., 2008; Arif and Abdullah, 2011; Wilson et al., 2012). Parrish et al. (2017a) report that the highest O_3 design values (the 3-year running mean of the annual 4th-highest peak daily 8-hour O_3 mixing ratio) in Southern California are converging toward of limit of 62.0 ± 1.9 ppb, which they identify as the O_3 design values that would result from U.S. background O_3 concentrations. Parrish et al. (2017b) report decreasing O_3 transported across the Pacific into the western U.S. after 2000. As noted, regional background O_3 in the southeastern U.S. does not appear to be trending either upward or downward, even though trends in background O_3 have been established in other areas or globally.

In the southeastern U.S., the simple conceptual model of O_3 transported into a study region across upwind boundaries is incomplete. High O_3 typically occurs during multi-day stagnation episodes, which are associated with the presence of high barometric pressure over the domain and limited transport (Blanchard et al., 2013). Transport distances determined from 24-hour back-trajectory computations are less then 300 km for the highest decile O_3 (Blanchard et al., 2013). Mean 24-hour transport distances are less than 350 km during June and less than 380 km during July (Blanchard et al., 2014). These distances are approximately equivalent to distances from Birmingham to Mobile, AL, or from Atlanta to Savannah, GA. Local and regional emissions can accumulate over multiple days and potentially could contribute to observed O_3 concentrations (e.g., aloft) that are considered as regional background. In contrast to emissions originating upwind, carryover from emission sources within the study domain is a manageable component of efforts to reduce O_3.

4.2 Seasonal Variations of O_3, NO_y, NO_z, HNO_3, and VOCs

The seasonal oscillations of monthly O_3 maxima in the Southeast are coupled to local or regional meteorology, solar radiation, and emissions (e.g., Blanchard et al., 2013; 2014; Hidy et al., 2014). ~~The meteorological factors having the strongest influence on daily peak 8-hour O_3 mixing ratios at SEARCH sites are~~ Variations of daily maximum temperature and mid-day relative humidity (RH)~~, whose~~ are associated with variations ~~cause~~ of daily peak 8-hour O_3 mixing ratios ~~to vary~~ by ~ ±30 percent from mean peak 8-hour O_3 mixing ratios, after also accounting for variations of other meteorological factors (Blanchard et al., 2014). Air mass back trajectories originating from the south (~ 150 to 200 degrees) exhibit peak 8-hour O_3 that is ~5 – 10 percent lower than average; daily peak O_3 decreases as 24-hour back trajectory distances increase from zero to ~600 km, consistent with association of higher O_3 concentrations with air mass stagnation rather than transport (Blanchard et al., 2013; 2014). At SEARCH sites, the monthly O_3 maxima (highest daily peak 8-hour O_3 each month) and mean daily peak 8-hour O_3 mixing ratios typically occurred in summer months, especially inland, and declined more than other monthly maxima (Figures 3 and 4). Summer means were not always higher than spring averages, especially at rural and coastal sites and during more recent years (Figure 4). Roughly constant winter monthly peak 8-hour maxima of ~40 ppbv occurred throughout the period of record (Figure 3). The seasonal variability of the highest peak daily 8-hour O_3 therefore declined over time (see also Table S3). Similar results were found for monthly means of hourly measurements, discussed in Section 4.3 on diurnal variations. Other recent studies have reported decreasing seasonal variability of O_3 across the U.S. using data from large numbers of monitoring sites (Chan, 2009; Chan and Vet, 2010; Cooper et al., 2012; Paoletti et al., 2014; Simon et al., 2015). Declines in seasonal variability are thought to result from changing rates of O_3 formation as precursor emissions have declined, or from increasing influence of intercontinental background O_3, not from changes in seasonal variations of temperature and other meteorological factors (Chan, 2009; Cooper et al., 2012; Simon et al., 2015). ~~With declining anthropogenic influence, background O_3 represents an increasingly important relative contribution. Background O_3 may also represent an increasing absolute contribution in our study area, as multiple studies have demonstrated increasing trends in global background O_3 mixing ratios (Ordóñez et al., 2007; Oltmans et al., 2008; Arif and Abdullah, 2011; Wilson et al., 2012).~~

The SEARCH data indicate that seasonal variations occur in ambient O_3, NO_y, NO_z, HNO_3, and the ratio of NO_z/NO_y (Figure 5). Seasonal variations of temperature and other meteorological factors are known to cause seasonal variations of O_3 and NO_y species concentrations. The monthly average NO_z and HNO_3 mixing ratios indicate that active photochemical processing of NO_x occurs during well more than half the year in the warm climate of the southeastern U.S.

~~Seasonal differences in mean mid-day (2 p.m.) hourly O_3 mixing ratios (selected to represent the average mid-point of the daily peak 8-hour O_3 maxima) are related in part to the extent of photochemical processing (Figure 5). At each site, the higher mean monthly 2 p.m. O_3 mixing ratios are associated with higher mean ratios of NO_z/NO_y. The lowest O_3 mixing ratios and~~

~~ratios of NO_z/NO_y tend to occur during winter (December – February), with increasing values during other months. This result indicates that, on average, greater O_3 formation and accumulation occurs when a larger fraction of NO_x has been converted to reaction products by early afternoon (Figure 5). At urban sites, mean NO_z/NO_y seldom exceeds ~0.6 due to ongoing emissions of NO_x, which indicates that further O_3 formation and accumulation would be possible with additional daytime hours for photochemical reactions to proceed. Similar results are obtained for comparison of mean 2 p.m. O_3 mixing ratios with mean ratios of HNO_3/NO_y. Additionally, higher mean monthly 2 p.m. O_3 mixing ratios are associated with higher mean mixing ratios of NO_z and of HNO_3.~~

~~The associations of O_3 with NO_z found in the observations are indicative of NO_x-oxidation reactions occurring in the presence of ambient VOCs, which provide a pool of free radical species that contribute to O_3 accumulation in both urban and rural areas.~~

The effects of VOC species on O_3 formation depend on both their ambient concentrations and their reactivities. To describe VOC variations at sites with long-term VOC measurements, we use isoprene data as an indicator of biogenic VOCs and toluene as an indicator of anthropogenic VOCs (nominally emitted as a gasoline vapor). The importance of isoprene emissions for O_3 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). We also consider other reactive VOC species of interest, including α-pinene (biogenic) as well as ethylene and xylenes (anthropogenic). Summer (June – August) months exhibit elevated ambient mixing ratios of rural and urban isoprene, typically about 5 – 10 ppbC, that are one to two orders of magnitude greater than those occurring between October and April (Figure 6). Transitions between low and high ambient isoprene mixing ratios occur in mid-May and mid-September in northern Georgia (Figure 6). Annual mean isoprene mixing ratios were relatively constant, ~2.5 – 3 ppbC, between 1998 and 2014. ~~OH reactivity, computed as the product of concentration and k_{OH}, indicates that b~~Biogenic VOCs, primarily isoprene, represent ~20% of the VOC reactivity at JST, ~30% at South Dekalb (SDK, located in metropolitan Atlanta ~16 km southeast of JST), and ~50% at YRK, averaged over all samples collected between 1999 and 2007 (Blanchard et al., 2010a). ~~Isoprene OH reactivity predominates at JST in summer but not in spring or fall (Figure 6).~~ Through precursor interactions, seasonal variations in isoprene mixing ratios are expected to affect seasonal variations in O_3 mixing ratios and production rates.

~~Alkenes and aromatic compounds (largely originating from motor vehicle and industrial process emissions) account, respectively, for ~20 – 40% and ~20% - 25% of the average VOC OH reactivity at JST, SDK, and YRK (Blanchard et al., 2010a).~~ Mean mixing ratios of ethylene and aromatic compounds vary substantially between urban and rural sites and exhibit less, and a different, seasonal variation than does isoprene, peaking in the fall rather than in the summer (compare Figures 6, S5, S6). Daily average mixing ratios of toluene, xylenes, and ethylene decline over the years, consistent with regulatory reductions of anthropogenic VOC emissions (Figures S5, S6). Seasonal variations in ambient mixing ratios and trends in the anthropogenic emissions of aromatic compounds are expected to influence O_3 mixing ratios and production in urban settings (rural anthropogenic VOC mixing ratios are lower but detectable).

The 24-hour average VOC mixing ratios are of somewhat limited value for showing the influence of VOCs on O_3 formation and accumulation. VOC influence is dependent on NO_x mixing ratios, which vary depending on proximity to emission sources and time of day. Meteorological variability, including diurnal and day-to-day changes in temperature, vertical mixing, cloud cover, photolysis, and air mass transport, further obscures the quantitative effects of VOCs on seasonal and interannual variations of O_3. Influences of anthropogenic VOCs at SEARCH sites have previously been reported (Blanchard et al., 2010b; 2014) and are not analyzed beyond this summary.

4.3 Diurnal Variations of O_3, NO_y, NO_z, and HNO_3

Summer (June – August) mean O_3 mixing ratios exhibit characteristic nocturnal minima and mid-day (noon to 4 p.m., midpoint ~ 2 p.m.) maxima at all SEARCH sites (Figure 7). This diurnal pattern remained essentially the same at both the urban and rural sites from 1999 through 2014, but the daytime maxima decreased. Between 1999 and 2014, the summer mean mid-day maxima declined by ~30 ppbv at all sites, while nocturnal means exhibited variable responses (Figure 7). Similar diurnal variations occur throughout the year, with smaller decreases in the mean mid-day O_3 maxima occurring during seasons other than summer (Figures S7 – S9). By the end of the study period, diurnal O_3 profiles were higher during spring (March through May) than summer at the rural sites (CTR and YRK, Figures S7 and S8), consistent with the reduction in summer mean monthly daily peak 8-hour O_3 averages (Figure 4). Decreasing summer diurnal mean NO_y, HNO_3, and NO_z mixing ratios were also observed, with a general flattening of the profiles and with the times of maxima remaining consistent (Figures S10-12). O_3 changes are discussed in relation to changes in NO_y and NO_z in Section 4.4, with emphasis on summer and additional consideration of spring months.

4.4 Observed Relationships between ~~Ozone Production Efficiency (OPE)~~ O_3 and NO_z

~~4.4.1 Linear Models~~

As discussed above, O_3 mixing ratios vary seasonally and diurnally in response to variations in emissions, weather, background O_3, and other factors. To reduce the influence of seasonal and diurnal variability, this section focuses on mixing ratios of NO_z, HNO_3, and O_3 at 2 p.m. during June and July. Both temperature and solar radiation are typically high during June and July, and multi-day stagnation events occur frequently in association with high barometric pressure (Blanchard et al., 2013). Exceptions exist during the passage of frontal systems (Blanchard et al., 2013; Figure S13). The 2 p.m. hour has the highest, or close to highest, average hourly O_3 for all sites and years (Figure 7). The atmosphere is well-mixed by mid-day. Over the range of ambient mixing ratios observed across 15 years, the June-July 2 p.m. O_3 values are distinctly nonlinear in relation to ambient NO_z and HNO_3 mixing ratios (Figure 8). More variability is evident at urban sites than at rural sites, consistent with ~~variable~~ influence of urban NO_x and perhaps VOC emissions on O_3. The nonlinearity indicated in Figure 8 is also evident when the data are restricted to days having the highest peak daily 8-hour O_3 mixing ratios (Figure S14). ~~We employ multiple approaches to account for nonlinearity and variability in using the data to estimate observed OPE. We use "observed" to distinguish between field data-based values and theoretically-based values. The former are affected by an ambiguity associated with deposition losses, discussed below.~~

4.4.1 Linear Models

Linear regressions are fit to the afternoon data by year, as shown in Figure 9 for 2013 and in Table S4 for all years. During multi-week periods within any summer, all sites exhibit near-linear relationships of mid-day O_3 to NO_z. Because the ranges of NO_x and NO_z mixing ratios within each year are limited, year-specific relationships are close to linear and linear models are statistically significant. ~~We use the slopes of the linear regressions of O_3 vs. NO_z as one set of estimates of year-specific and site-specific observed OPE.~~ Steeper slopes at rural sites than at urban sites in Figure 9 ~~indicates~~ suggest that either more O_3 molecules formed per molecule of NO_x consumed in rural locales than in urban areas, or that greater losses of NO_z occurred at the rural sites~~,~~ as discussed below. At all sites, similar results are obtained for regressions of O_x ($O_3 + NO_2$) vs NO_z compared with O_3 vs NO_z (Figure 9, caption). At 2 p.m., rural O_3 mixing ratios are nearly identical with O_x mixing ratios and with other metrics (e.g., O_3 – [NO_y – NO]) (Figure S15~~3~~). At urban sites, 2 p.m. NO_2 mixing ratios are non-negligible, but this difference alters the intercepts rather than the slopes of the regressions of O_x vs NO_z compared with O_3 vs NO_z (Figure 9). As previously noted (Figure S13), even during the two-month periods that we analyzed, the weather is not always conducive to O_3 formation and such days could influence the observed slopes and intercepts. However, regression results restricted to days with weather that favors O_3 formation (as defined in Figure 9) do not differ from the unrestricted regressions.

Plotting the year-specific (June – July) computed ~~observed OPE (~~regression slopes~~)~~ versus mean June – July 2 p.m. NO_z shows ~~that OPE has~~significant increases over time ~~increased~~ as ambient NO_z mixing ratios have decreased, subject to year-to-year variability (Figure 10, Table S4). Similar urban-rural differences and patterns of increasing ~~OPE~~ regression slopes are also observed when data are restricted to March and April (spring) at YRK and JST (Figure S16~~4~~). The results for spring show more variability than the summer year-specific linear models~~, but nonetheless indicate that in spring fewer O_3 molecules formed per molecule of NO_x consumed compared to summer~~. One key difference between spring and summer days is that cumulative solar radiation between sunrise and 2 p.m. is greater on summer days than on spring days, presumably fostering greater photochemical extent of reaction and accumulation of O_3 during summer.

The regression slopes determined from 2 p.m. data could ~~be biased high as estimates of observed OPE~~reflect day-to-day differences in transported O_3 if background O_3 is consistently higher on high-O_3 days than on low-O_3 days and NO_z is not (in contrast, random variations in day-to-day background O_3 and NO_z would~~, in contrast,~~ introduce variations, or scatter, around the regression lines). We checked for ~~potential bias~~an effect of this type by repeating the analyses using differences in mixing ratios. Two sets of difference-based regressions are used: (1) the differences between 2 p.m. and 10 a.m. hourly measurements, and (2) the differences between 11 a.m. and 10 a.m. hourly measurements. The differences are computed for each day to minimize or eliminate the unknown day-specific background levels, and are then used in the regressions. These hours were selected to focus on times of day when the atmosphere is well-mixed. The morning rise in mixing heights is expected to contribute to increases in the mixing ratios of secondary species as aged air aloft is incorporated into the mixed layer. The most rapid rates of increase in diurnally-averaged O_3, NO_z, and HNO_3 values occur between ~8 a.m. and 12 noon local time (Figures 7, S8 – S9). By mid- to late-morning hours during summer, considerable vertical entrainment has occurred, and subsequent changes in the mixing ratios of secondary species likely reflect same-day atmospheric chemical reactions. Computing afternoon – morning differences and late morning – mid-morning differences helps account for day-to-day variations in regional background O_3, but also introduces higher relative uncertainties because four measurements (two differences) are used in the regressions. Results for all three approaches are tabulated in Table S5, by site and year. Like the regressions based on 2 p.m. measurements, the difference-based regressions indicate that observed ~~OPE has~~slopes have increased over time (Table S5~~, Figures S15 – 17~~). ~~The best statistical fits are for the regressions using non-differenced afternoon data.~~ The difference-based regressions exhibit lower slopes than the non-differenced afternoon regressions, which could be due to lesser statistical fit, or to better accounting for regional background O_3, or to a combination of these factors. The difference-based regressions suggest that O_3-NO_z ~~the observed OPE~~slopes increased from less than 5:1 in the late 1990s and early 2000s to values between 5:1 and 10:1 after 2010 (~~Figures S15 – S17;~~ Table S5). These lower slope values are consistent with our previous results in which observed ~~OPE~~O_3-NO_z relationships ~~was~~ were determined while also accounting for day-to-day variations in meteorology, which indicated that ~~within the range of 1 to 5 ppbv NO_z,~~ JST, YRK, and CTR O_3/NO_z slopes were 3.5, 5.0, and 7.1, respectively, within the range of 1 to 5 ppbv NO_z, for measurements made during March – October of 2002 - 2011 (Blanchard et al., 2014).

A second potential ~~bias~~ effect on the temporal changes in the regression slopes could ~~result from~~be due to changes in NO_2 measurement methods, previously described; this possibility was checked by using regressions of O_3 vs. HNO_3 (Figure S17~~18~~). The results indicate that the relationship in Figure 10 is not an artifact of changes in NO_2 measurement methods. The record is more complete for the regressions of O_3 vs. HNO_3, because the HNO_3 measurements were made over a longer time than the NO_2 measurements (and the latter are needed for computing NO_z). As shown for YRK, the year-specific slopes of 2 p.m. O_3 vs. NO_z and for O_3 vs. HNO_3 each increased substantially after about 2008 (Figures 10, S17~~18~~). The O_3 vs. NO_z and O_3 vs. HNO_3 regression slopes tend to level out after 2011, and possibly decrease somewhat, but variability is too high to project beyond the observed data ranges (Figures 10, S17~~18~~). Similar results are obtained for spring for JST and YRK (Figures S18~~19~~ and S19~~20~~).

Our increases in year-specific slopes of O_3 versus NO_z potentially could be due to increasing losses of NO_z species, especially HNO_3, over the long-term SEARCH record. As previously noted, however, the CASTNet data show declining rates of both wet and dry nitrate deposition since the late 1990s, with no change in the ratio of deposition to emissions (Figure 1). Therefore, the long-term slope increases cannot be attributed to increasing deposition losses of HNO_3 (whether absolute or fractional). Qualitatively, the CASTNet data suggest that the observed slopes would likely be at least a factor of two smaller if adjusted for deposition losses. This adjustment would be comparable to the 1990s studies discussed in Section 4.4.2.

In Figure 9, the intercepts of year-specific regressions for 2013 approach 20 ppbv O_3, which could be interpreted as a regional background O_3 level relatively unaffected by local chemistry. These values are lower than those in Figure 2 and lower than the estimated range of 48 ppbv to 59 ppbv for air transported into the Houston area. They are also lower than ~~-~~modeled western non-U.S.-anthropogenic ~~-~~regional background O_3 levels of ~ 40 – 50 ppbv (Lefohn et al., 2014; Dolwick et al., 2015) but are consistent with model estimates of non-U.S.-anthropogenic ~~-~~background O_3 less than ~30 ppbv in Atlanta (Lefohn et al., 2014).

Since regression intercepts restricted to days with weather that favors O_3 formation do not differ much from the intercepts of the unrestricted regressions (Figure 9), our low intercepts for recent years do not appear to be linked to meteorological conditions that specifically favor O_3 loss over formation. However, when considered over the full set of years, the O_3-NO_z relationships on the highest O_3 days differ from those on larger subsets of the data (Figure S14). Possibly, the intercept terms cannot be fully interpreted without additional consideration of O_3 carryover in multiday episodes, as previously noted. The intercept terms for earlier years are higher than for later years; for example, the intercepts for the YRK regressions range from 27 ± 3 to 42 ± 4 ppbv prior to 2009 (for all but two of these years, intercepts are 36 – 38 ppbv). The intercept terms for earlier years are consistent with 1997 – 2006 eastern U.S. summer baseline O_3 levels (32 ± 12 ppbv in the absence of continental influences) reported by Chan and Vet (2010).

Higher intercepts during early years ~~are associated with lower OPE, and~~ could be due to fitting a linear regression to the upper portion or the mid-range of the nonlinear relationship between O_3 and NO_z, as shown in Figures 8 and S14. The nonlinearity and the downward trends in mean NO_z and HNO_3 mixing ratios mean that slopes of regressions computed at higher mean NO_z and HNO_3 mixing ratios should not be extrapolated beyond their range of applicability to the y-intercept. Alternatively, the trend toward lower intercepts could reflect declining mixing ratios upwind of the study sites, consistent with documented long-term reductions of ambient O_3 mixing ratios throughout the U.S. (e.g., Chan and Vet, 2010; Lefohn et al., 2010; Paoletti, 2014; Simon et al., 2015; Hidy and Blanchard, 2015). As previously discussed, however, regional background O_3 in the southeastern U.S. does not appear to be trending either upward or downward,

~~As discussed next, previous studies obtained lower OPE values after adjusting for deposition losses. While such corrections could be applied to our observed OPE values, we instead ask whether our apparent increase in observed OPE could be due to increasing losses of NO_z species, especially HNO_3, over the long-term SEARCH record, rather than to increasing production efficiency. As previously noted, however, the CASTNet data show declining rates of both wet and dry nitrate deposition since the late 1990s, with no change in the ratio of deposition to emissions (Figure 1). Therefore, the long-term increase in observed OPE cannot be attributed to increasing deposition losses of HNO_3 (whether absolute or fractional). Qualitatively, the CASTNet data suggest that the observed OPEs would likely be at least a factor of two smaller if adjusted for deposition losses. This adjustment would be comparable to the 1990s studies discussed below, which yielded unadjusted OPEs of ~5:1 to 11:1 compared with OPEs of ~3:1 to 5:1 when adjusted for deposition.~~

4.4.2 Comparisons with Observational~~ed~~ and Modeling Results~~ed~~ ~~OPE~~

The preceding section demonstrates that the slopes of the regressions of O_3 versus NO_z increased over time and examines the potential influence of measurement artifacts, weather, deposition, and pollutant transport on the results; none of these plausible influences adequately explains why the slopes of the regressions of O_3 versus NO_z increased. The increasing slopes appear to indicate that relationships between O_3 and NO_z changed over time, yet the physical processes associated with the changes remain ambiguous. Modeling studies offer insights. Modeling process analysis by Reynolds et al. (2004) for the eastern U.S. predicted that the number of NO cycles (i.e., the ratio of new plus recreated NO to new NO) would increase from 8 to 14

(~75%) in central (metropolitan) Atlanta and from 9 to 11 (~20%) northwest of Atlanta in response to a 60% reduction of NO_x emissions from a 1996 emissions base case. Both the modeled emission reduction (60%; compare to Figure 2) and the modeling subregions (central Atlanta, JST; northwest Atlanta, YRK) are directly comparable to our study period and domain. NO cycling is relevant to our regressions of O_3 versus NO_z because an O_3 molecule is produced, with some loss, each time NO cycles through a set of reactions until NO cycling terminates in reactions products that are components of NO_z (e.g., HNO_3, PAN). Thus, the observed increases in the slopes of the regressions of O_3 versus NO_z are directionally consistent with modeling predictions, but are larger than the predicted 20 – 75% increases in NO cycling.

The data were selected to represent periods that have consistent weather from day to day to minimize the influence of meteorological variability, and regressions of subsets of the data yield slopes and intercepts comparable to those based on all days of June and July (Figure 9). However, the observed O_3 decreases that have occurred in the region (Figures 2 and 3) could not have occurred if O_3 formation rates increased by factors of ~3 to 4 (as suggested by Figure 10), or even by a factor of two (Table S5), since NO_x emissions declined by ~60%, or ~5% per year over 20 years (Figure 1; Hidy et al., 2014). This consideration suggests that increased NO cycling, while likely linked with our observational results, cannot be the only factor involved. The regression slopes are nonetheless consistent with related studies when a basis for comparison exists.

The SEARCH observed afternoon ~~OPE~~ slope values of ~5:1 prior to 2003 – 2007 are comparable to, or lower than, similar regression results obtained in studies during the 1990s, which showed observed summer ~~OPE~~ slope values of 11:1 in rural Georgia in 1991 (Kleinman et al., 1994), 8.5:1 at rural eastern sites (Trainer et al., 1993), 7:1 near Birmingham, AL in 1992 (Trainer et al., 1995), 5.7:1 near Nashville, TN in 1995 (Sillman et al., 1998), and 4.7:1 near Nashville, TN, in 1999 (Zaveri et al., 2003), and to modeling results and observations with composite ~~OPE~~ regression slope values of 6.7 and 7.6, respectively, within the afternoon planetary boundary layer in the eastern U.S. during the summer of 2002 (Godowitch et al., 2011) The SEARCH regression ~~OPE~~ slope values prior to 2003 – 2007 are, as expected, higher than other 1990s ~~OPE~~ values that were corrected for deposition losses, which, for example, yielded adjusted estimated ~~OPE~~ values between 3:1 and 5:1 near Nashville in 1995 (Nunnermacker et al., 1998; St John et al., 1998; Sillman et al., 1998). Our higher observed ~~OPE~~ slope values after 2010 are consistent with aircraft measurements made in the Southeast in August and September 2013, which show O_x (= O_3 + NO_2) versus NO_z slope of 17.4, and they are also consistent with model calculations, which show slopes of 14.1 to 16.7 (Travis et al., 2016). Consistent with our regressions, Travis et al. (2016) did not adjust for variations in background O_3 and NO_z. For comparability, we note that our O_3 versus NO_z regression slopes were 13.1 to 18.8 (± 1.2 to 1.4) in June and July, 2013, at three of four sites (25.7 ± 2.8 at the fourth site, which is the most rural in character) and our O_x versus NO_z slopes were 12.0 to 18.9 (± 1.2 to 1.4) at three of the four sites (25.8 ± 2.8 at the fourth site). The increase in recently observed ~~OPE~~ slope values that we report is therefore supported by the 2013 data of Travis et al. (2016). Our apparently high ~~OPE~~ regression slope values are ~~also consistent with~~comparable to observations~~-based OPE~~ that averaged 12.9 in ship plumes and 33.5 in assumed background marine air, as reported by Kim et al. (2016) using data from a 2002 study of ship emission plumes off the coast of southern California, though the specific conditions associated with these two studies are different from ours and thus limit the applicability of the comparisons.

The increase in ~~OPE~~ regression slopes with decreasing ambient NO$_x$ and NO$_z$ is also directionally consistent with computations by Liu et al. (1987), which showed ~~relatively constant summer~~increasing OPE ~~of ~ 7 - 10 for ambient NO$_x$ exceeding ~7 ppbv, increases in OPE to ~20 as NO$_x$ declines from ~7 to ~1 ppbv, more rapid increases in OPE to ~60 as NO$_x$ further declines to ~0.1 ppbv, and a final slower increase of OPE to ~80~~ as NO$_x$ declines~~ to ~0.01 ppbv~~. ~~While t~~The numerical results of the modeling calculations by Liu et al. (1987) are specific to the modeled conditions, which represented complete oxidation of VOCs over a period of months. However, increases~~ing~~ in model-predicted NO$_x$ OPE with declining NO$_x$ results from multiple factors~~ that are pertinent to other conditions~~, such as radical reactions involving VOCs and NO$_x$~~,~~, that are pertinent to other situations (Lin et al., 1988).

In contrast to southern California, where Pollack et al. (2013) reported a shift from PAN to HNO$_3$ production~~ with no change in OPE~~, the SEARCH data ~~exhibit an increase in observed OPE and~~ do not definitively show a changing fraction of HNO$_3$ relative to NO$_y$. Increasing formation of PAN (which regenerates NO$_2$) and decreasing formation of HNO$_3$ (which terminates cycling between NO and NO$_2$) could ~~increase OPE or otherwise~~ facilitate O$_3$ accumulation as ambient NO$_x$ and NO$_z$ mixing ratios continue to decline. Since the long-term SEARCH data record does not include measurements of PAN, this possible effect could not be investigated.

~~4.4.3 Future O$_3$ Responses~~5 Implications

~~Where NO$_x$ limits reaction rates, O$_3$ production is the product of OPE and ambient NO$_x$ mixing ratios as determined for specific ambient conditions (Liu et al., 1987), so O$_3$ reductions depend on changes in both OPE and NO$_x$. Increasing OPE offsets decreasing mixing ratios of NO$_x$, at least in part, so that O$_3$ reductions are less than proportional to NO$_x$ emission reductions. At present, there is no clear indication from the SEARCH data that OPE will continue to increase, begin decreasing, or level off. SEARCH data do not indicate that OPE has declined in recent years.~~ The trends in, and relationships between, O$_3$ and NO$_y$ species provide some insight into the potential for future O$_3$ changes in the southeastern U.S. The post-1990s O$_3$ trend provides one guide to future average rates of O$_3$ reduction in the sense that the rates of O$_3$ 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 even decreases somewhat, as indicated in Figure 10 for the years since about 2009. If OPE were to increase faster than NO$_x$ mixing ratios decreased, O$_3$ maxima would tend to increase with declining NO$_x$. If OPE were to start declining as NO$_x$ emissions and mixing ratios continue to decrease, O$_3$ maxima would decline less dramatically in the next few years compared with the past 6 - 7 years. At the limit of OPE approaching zero, O$_3$ maxima would level off and no further O$_3$ reductions would occur. From the observations to date, this condition appears to be well below ambient NO$_z$ levels of ~0.2 ppbv. Previous work indicates that VOC reactivity and O$_3$ losses contribute to nonlinearity; at ambient NO$_x$ mixing ratios less than ~0.4 ppbv, O$_3$ loss suppresses OPE, and below ~80 pptv NO$_x$, OPE becomes negative (Lin et al., 1988). The future O$_3$-NO$_z$ relationships are contingent on continuing an unspecified historical response to VOC changes.~~ Anthropogenic NO$_x$ and VOC emissions are each expected to continue to decline. Anthropogenic VOC mixing ratios have declined since 1999, but natural components such as isoprene and terpene mixing ratios have remained relatively constant (Figure 6; Blanchard et al., 2010a; Hidy et al., 2014), leaving ambient VOC levels increasingly dependent on biogenic emissions. Evidence suggests that O_3 formation in the SEARCH region will move toward more NO_x sensitive conditions with continued decreases in NO_x ~~emissions~~ and ~~more limited declines in~~ anthropogenic VOC emissions, coupled with high levels of natural VOC emissions in the region. This anticipated emission reduction path should reinforce the O_3-NO_z relationships and the ~~OPE~~ interpretation presented here.

~~5~~6 Conclusions

~~Summer O_3 mixing ratios declined along with decreasing emissions in the southeastern U.S. between 1999 and 2014. The seasonal variability of the highest peak daily 8-hour O_3 mixing ratios also declined over time: summer monthly O_3 maxima declined more than other monthly maxima, while winter monthly maxima of ~40 ppbv occurred throughout the period of record.~~ The seasonal differences in the past O_3 response to NO_x emission reductions ~~exhibits seasonal variability, which will~~ could have ~~potentially important~~ implications for future O_3 management if spring and autumn O_3 maxima fail to decline and thereby become a focus of concern that merits attention comparable to summer O_3 maxima.~~Higher mean monthly 2 p.m. O_3 mixing ratios are associated with higher mean ratios of NO_z/NO_y, indicating that more O_3 formation and accumulation occurs when more NO_x has been converted to reaction products by early afternoon, especially for mean NO_z/NO_y exceeding ~0.6. Higher mean mid-day O_3 mixing ratios and higher ratios of mean NO_z/NO_y occur in summer compared to other seasons.~~

The ~~summer O_3 trend is less than 1:1 proportional to precursor changes, as indicated by~~ observed relationships of O_3 to NO_z, which is the product of reactions involving NO_x~~.~~ , ~~Observationally-determined OPE increases as ambient mixing ratios of NO_x oxidation products decline, partially offsetting precursor decreases and contributing to the~~ are nonlinear ~~O_3 response, but also~~and suggest~~ing~~ increasing responsiveness of O_3 to NO_x~~.~~ over the study period. ~~The effectiveness of ongoing NO_x emission reductions on peak O_3 values will depend on the balance between changes in observed OPE and ambient NO_x, in the context of ongoing VOC changes.~~ In addition, changes in the relative importance of chemical reactions that yield HNO_3 compared with PAN are likely to play a role in altering ~~OPE and~~ O_3 accumulation. ~~The past O_3 response to NO_x emission reductions exhibits seasonal variability, which will have potentially important implications for future O_3 management if spring and autumn O_3 maxima fail to decline and thereby become a focus of concern that merits attention comparable to summer O_3 maxima.~~ Long-term documentation and analysis of trends in O_3 mixing ratios in relation to NO_x emission reductions and decreases in ambient reactive nitrogen (NO_y) concentrations yields opportunities for obtaining insights about ambient O_3 reductions that complement and corroborate air quality modeling predictions and add substantially to the “weight-of-evidence” approach for air quality management adopted by the U.S. government after 2000.

Data Availability

The SEARCH data are available at https://www.dropbox.com/sh/o9hxoa4wlo97zpe/AACbm6LetQowrpUgX4vUxnoDa?dl=0. EPA data are available at http://aqsdr1.epa.gov/aqsweb/aqstmp/airdata/download_files.html and at https://www.epa.gov/castnet.

Author Contributions

C. L. B. and G. M. H. designed the study and wrote the manuscript. C. L. B. carried out the statistical analyses.

Competing Interests

The authors declare that they have no conflict of interest.

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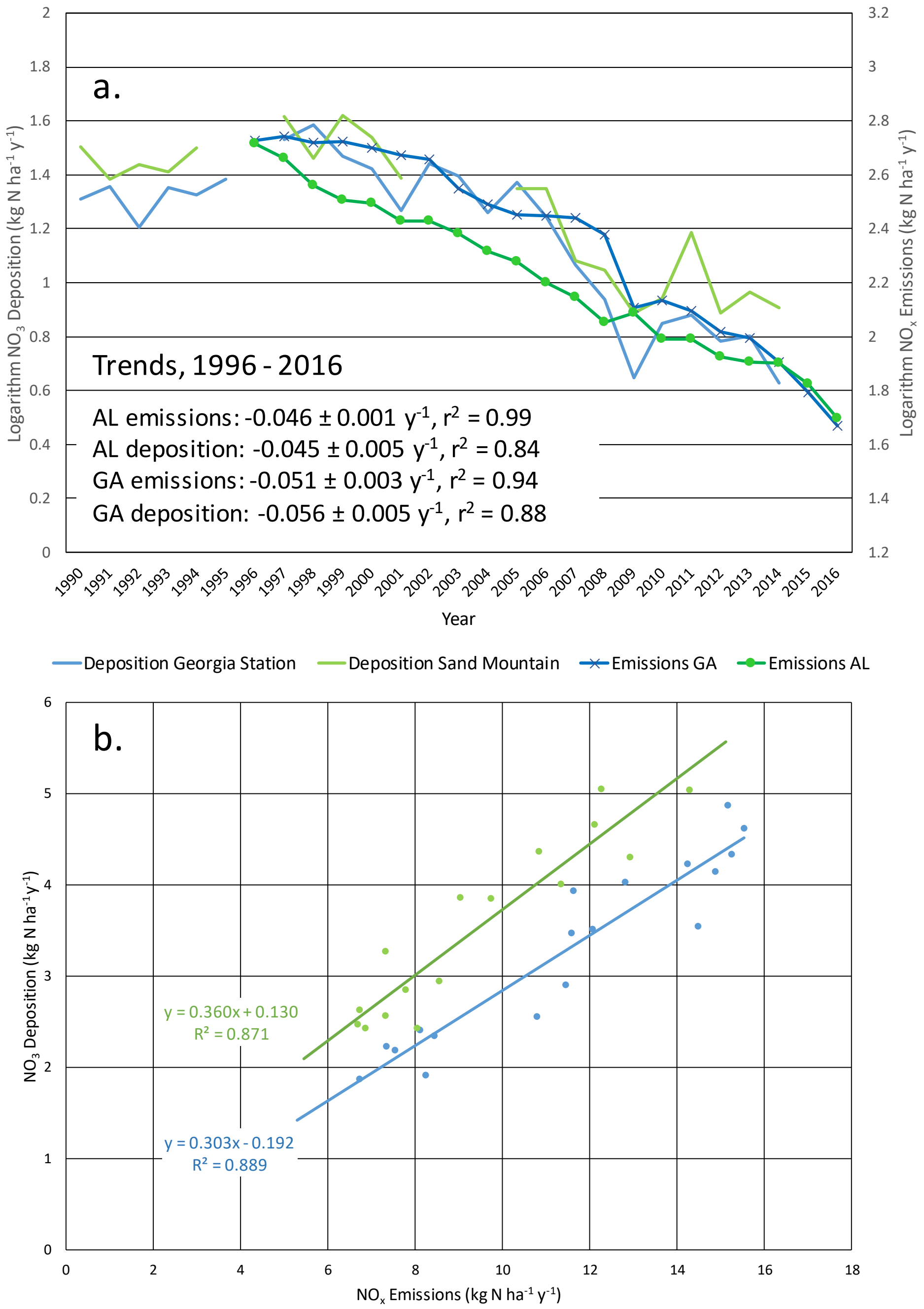


Figure 1. Comparison of nitrate deposition (wet plus dry) to NO$_x$ emission densities in Georgia and Alabama as (a) temporal trends and (b) regression of deposition against emissions (with same color coding in both panels). Nitrate deposition and NO$_x$ emission densities are expressed as kg ha^{-1} y^{-1}. NO$_x$ emissions are from all source sectors (supplement). Panel (a) shows natural logarithms vs. year and indicates that emissions and deposition trended downward at the same rates. Panel (b) s~~S~~lopes are statistically significant ($p < 0.0001$) and intercepts are not ($p > 0.1$).

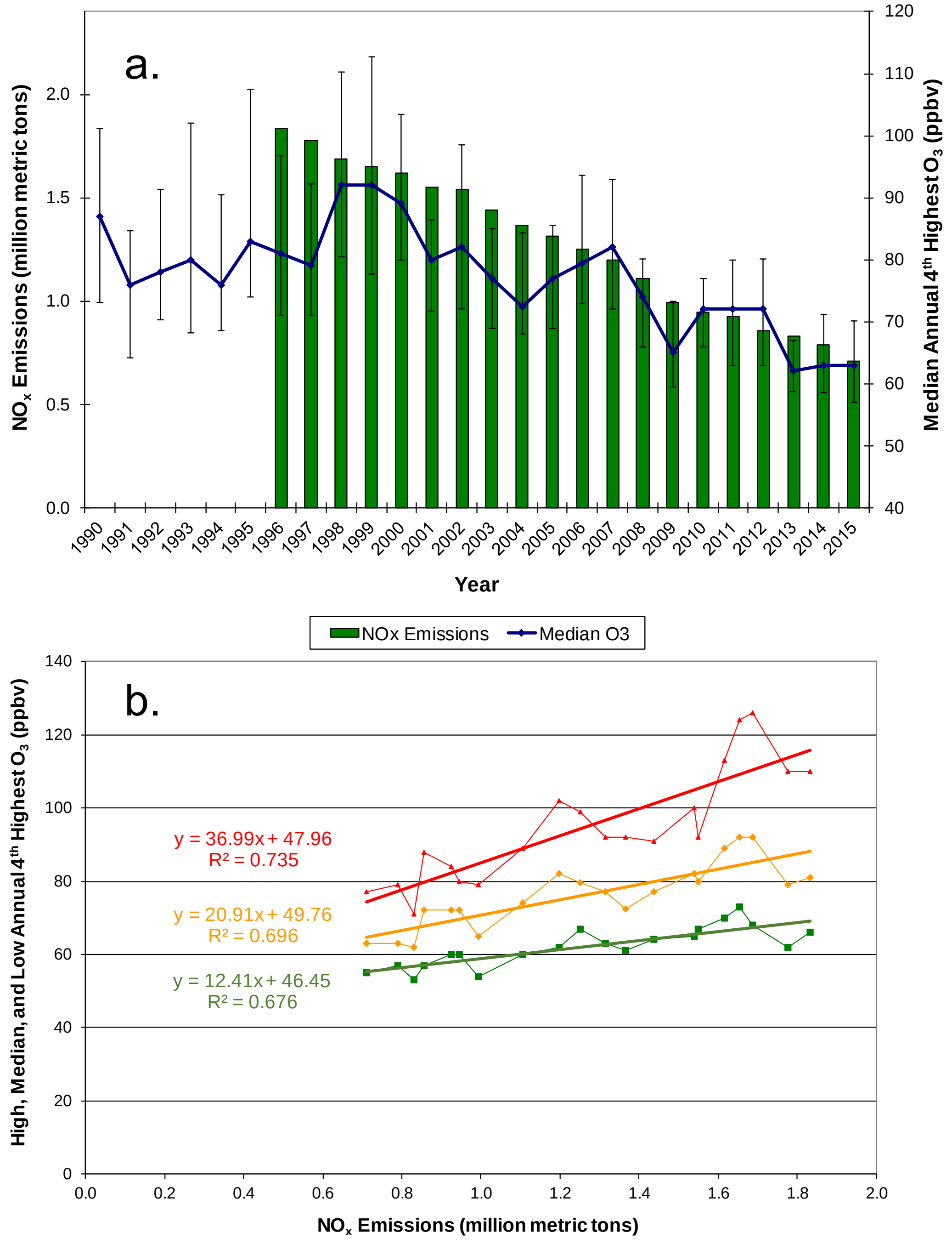


Figure 2. Comparison of annual 4th-highest daily peak 8-hour O_3 to NO_x emissions in Georgia and Alabama (a) trends (~~+~~± 90th ~~percentile site, ~~and10th percentile sites) and (b) regressions (high = 90th percentile site, median, and low = 10th percentile site annual 4th-highest daily peak 8-hour O_3). NO_x emissions are from all source sectors (supplement). O_3 data include all EPA AQS monitors in Georgia and Alabama for each year having at least 75% data completeness (mean = 55 monitors, low of 32 – 36 in 1990 – 1993). Slopes and intercepts are statistically significant ($p < 0.0001$).

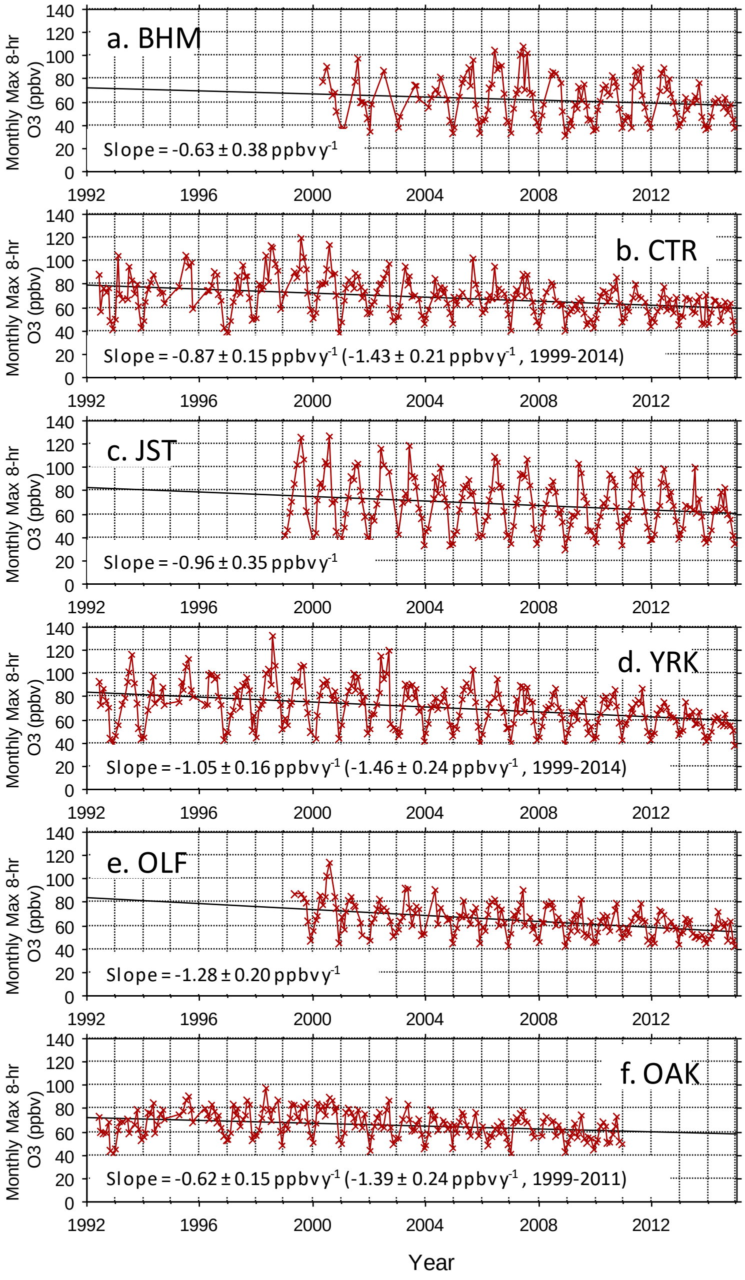


Figure 3. Monthly maxima of daily peak 8-hour average O_3 mixing ratios. All monthly maxima are determined from 24 or more days with 18 or more sampling hours per day. PNS and GFP (not shown) exhibit trends of -1.64 ± 0.45 and -0.60 ± 0.32 ppbv y^{-1}, respectively. Trends are statistically significant ($p < 0.01$) at CTR, JST, OAK, OLF, PNS, and YRK.

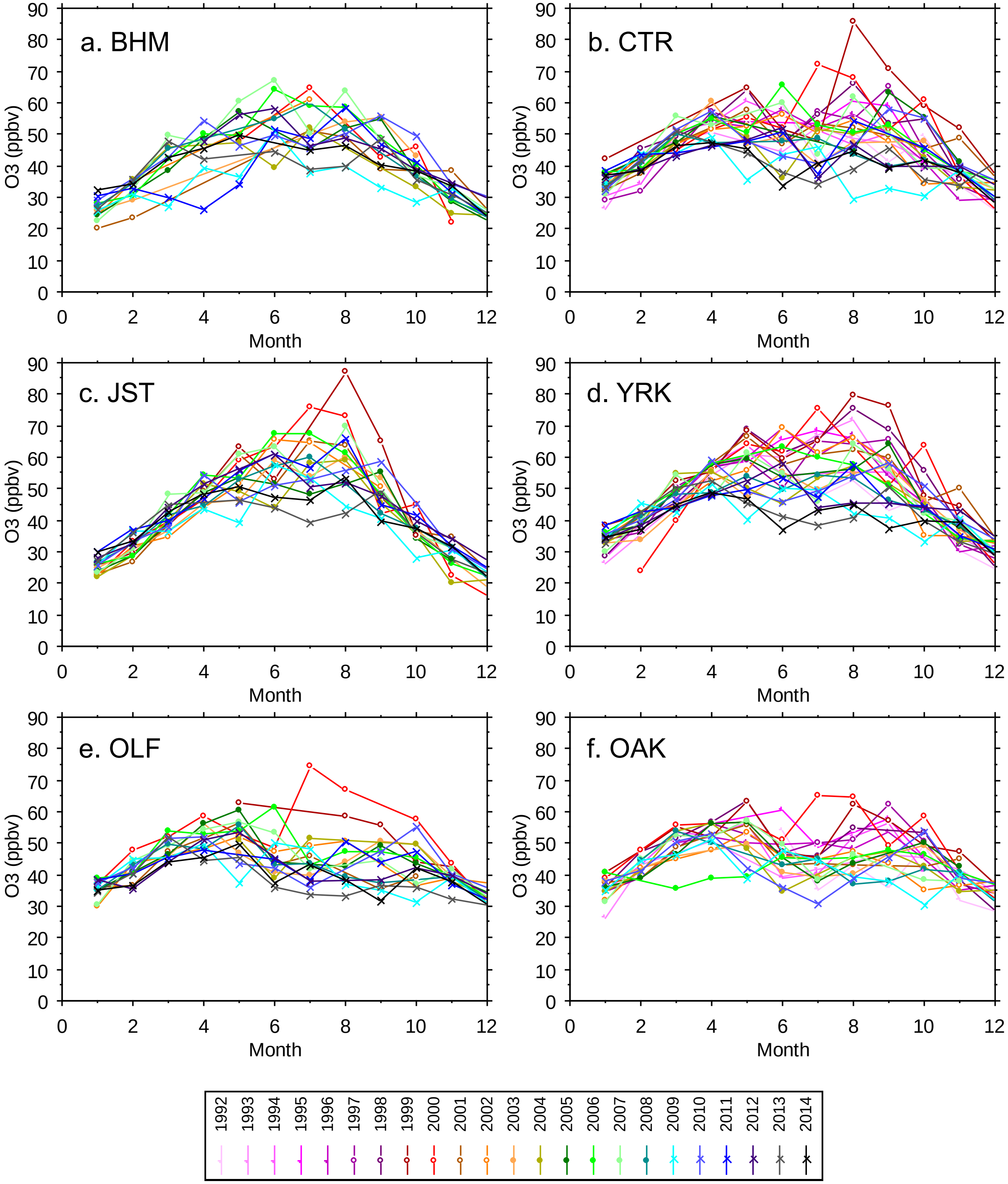
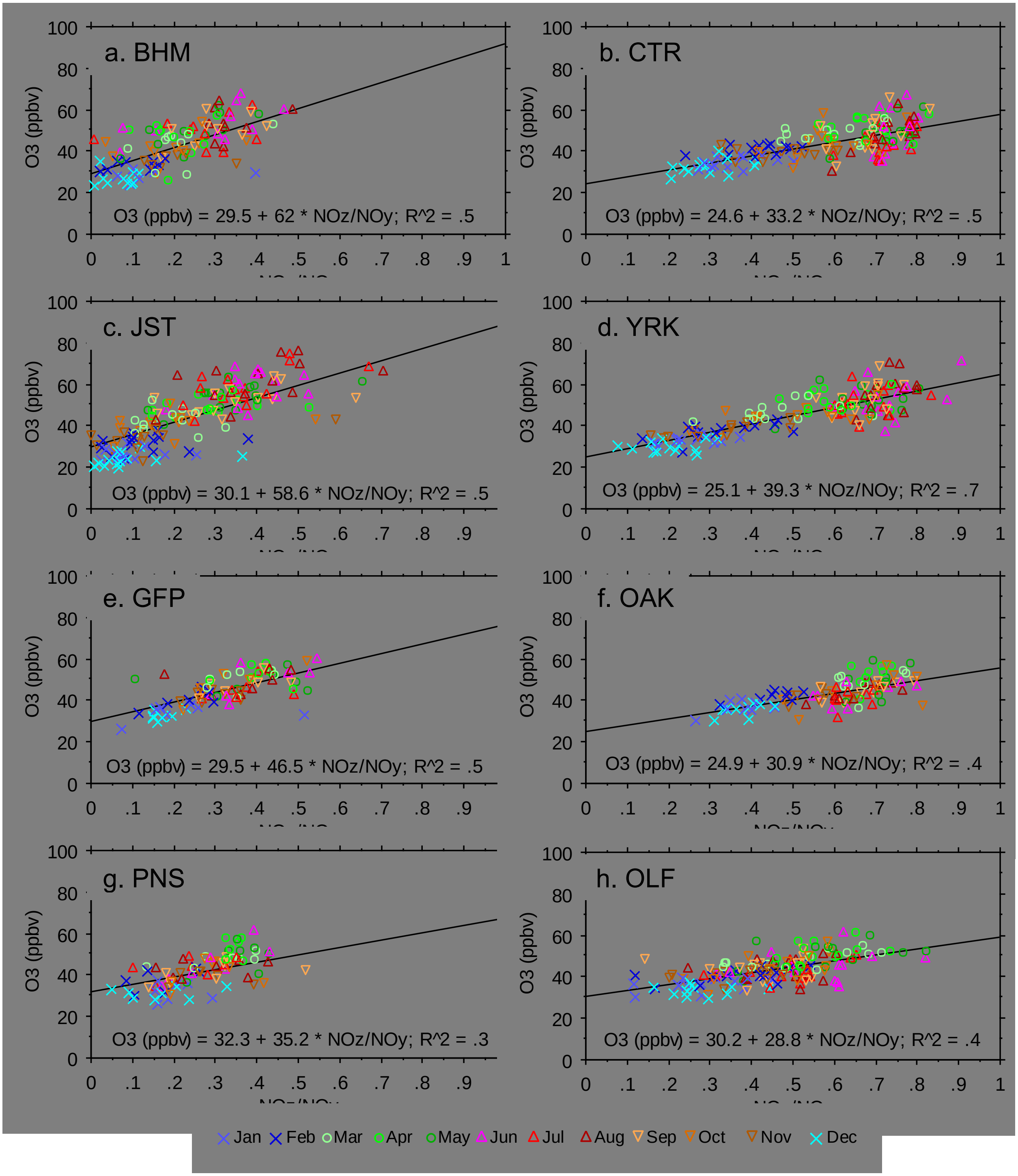


Figure 4. Monthly means of daily peak 8-hour average O_3 mixing ratios. All monthly means are determined from 24 or more days with 18 or more sampling hours per day. Standard errors of the means average 2 (range 0.8 – 5) ppbv.



~~Figure 5. Mean monthly 2 p.m O_3 vs. mean monthly 2 p.m NO_z/NO_y, 1999 – 2014. Each symbol is the monthly mean for one year. Standard errors of the monthly means average 2.5 ppbv O_3 and 0.075 (dimensionless) NO_z/NO_y. Linear regression yields site-dependent slopes of 31 – 62 ppbv O_3 per unit NO_z/NO_y (statistically significant, $p < 0.0001$).~~

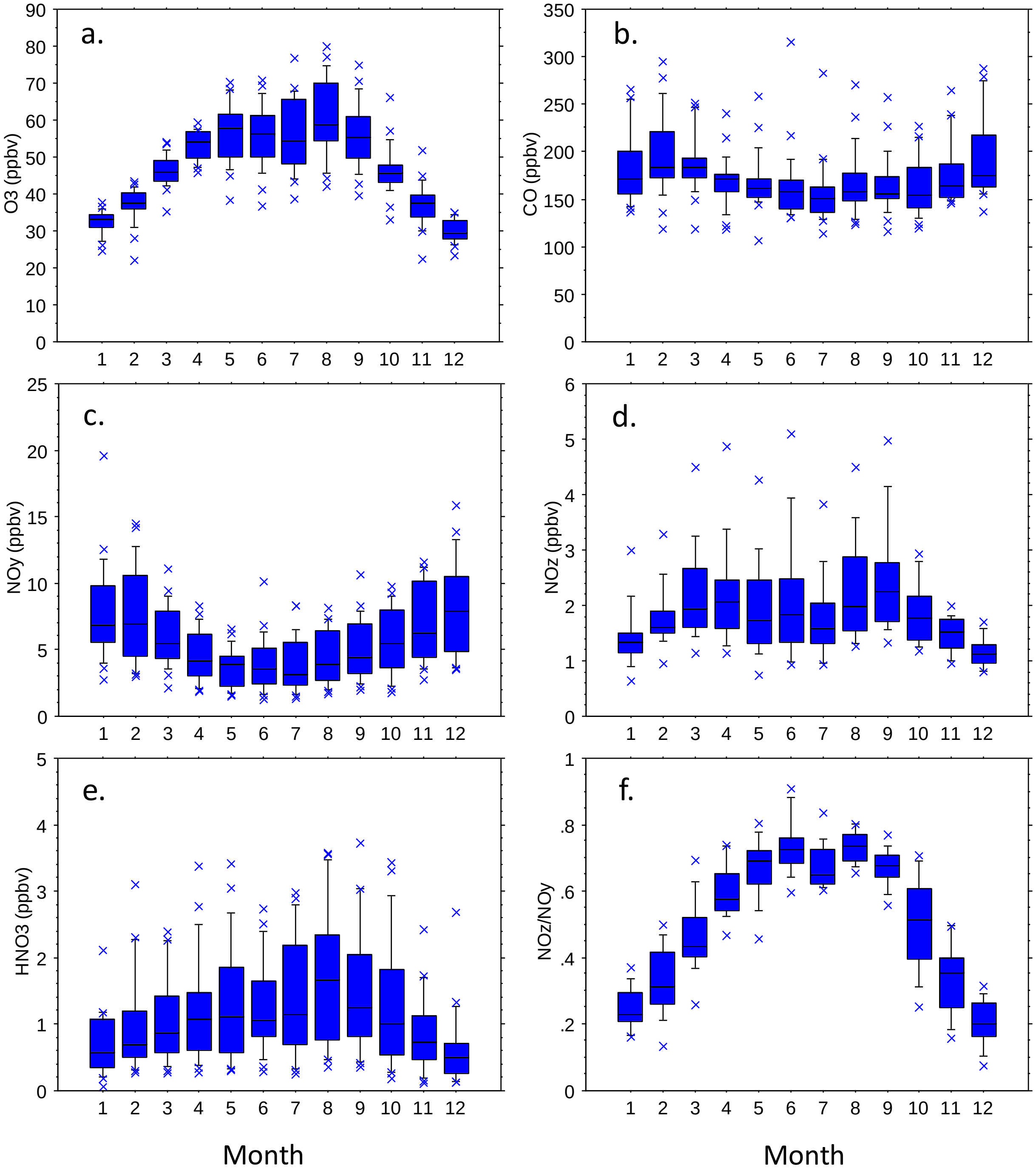


Figure 5. Statistical distributions of mean monthly species mixing ratios, all SEARCH sites, 1992 – 2014. Distributions indicate the 10th, 25th, 50th, 75th, and 90th percentiles of the monthly averages.

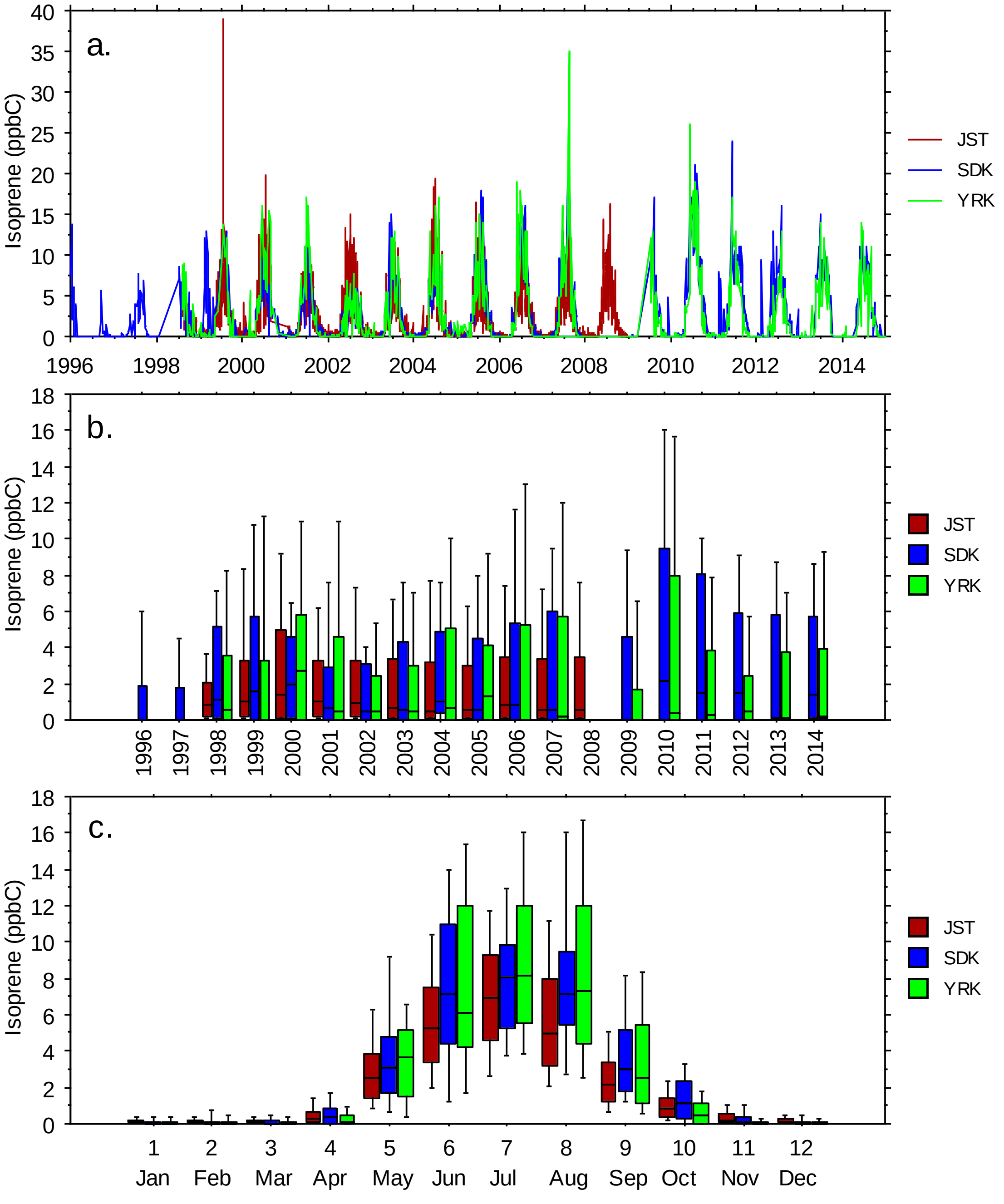


Figure 6. (a) Daily-average isoprene mixing ratios vs. date, (b) statistical distributions of daily-average isoprene mixing ratios vs. year, and (c) statistical distributions of daily-average isoprene mixing ratios vs. month~~, and (d) JST OH reactivity of isoprene and other compounds~~. Samples were obtained every day at JST and once every six days at YRK and SDK (Blanchard et al., 2010). Distributions indicate the 10th, 25th, 50th, 75th, and 90th percentiles. ~~OH reactivity is the product of concentration and rate constant, k~~$_{OH}$~~.~~

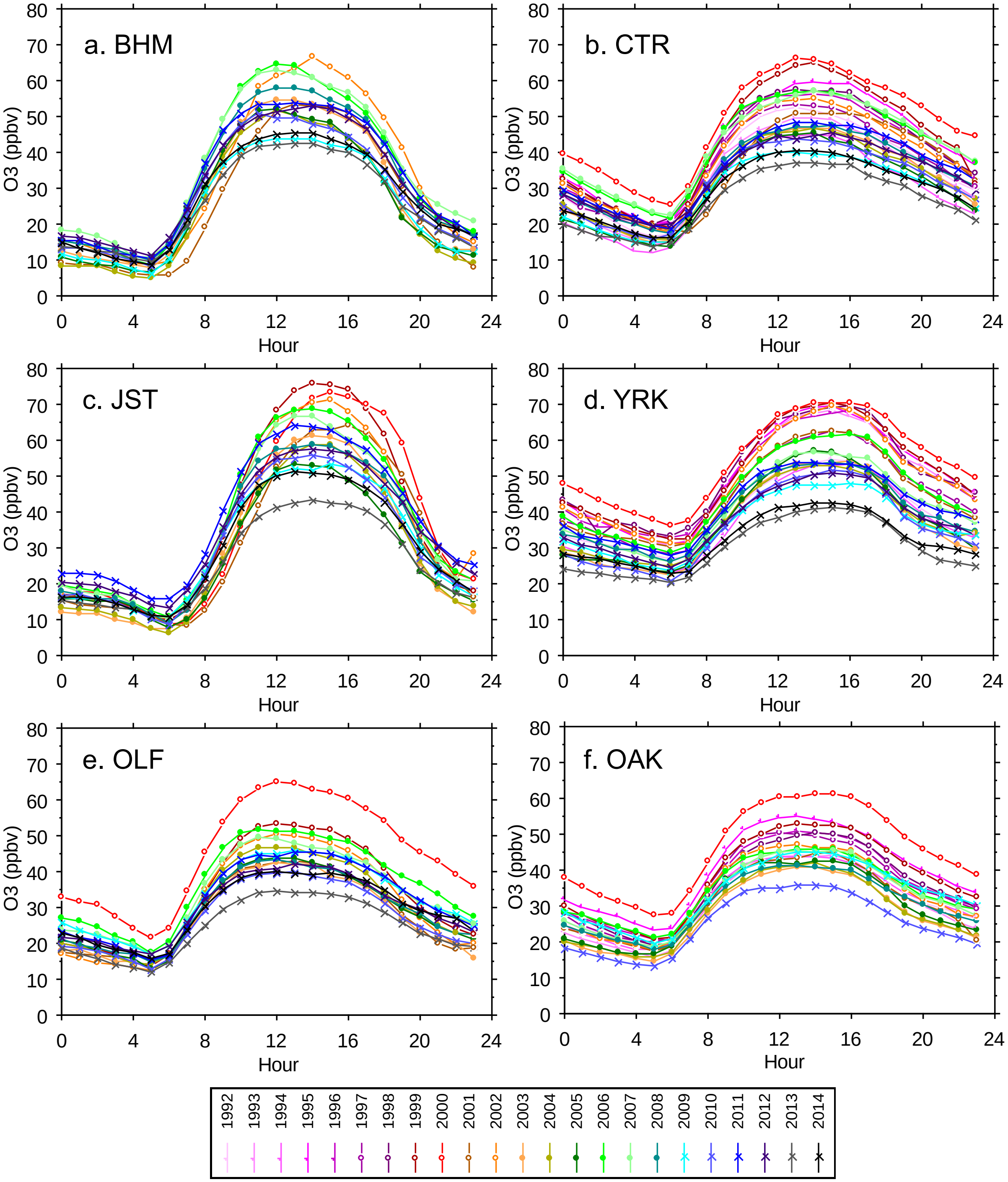


Figure 7. Average O_3 mixing ratios vs. hour, by year. Each data point is the mean of all hourly measurements during June through August. Sites at PNS and GFP (not shown) exhibit similar diurnal profiles and trends (sampling at those sites ended after 2009 and 2012, respectively). Standard errors of the means are 0.3 – 4 ppbv, ~2% of mean O_3 mixing ratios.

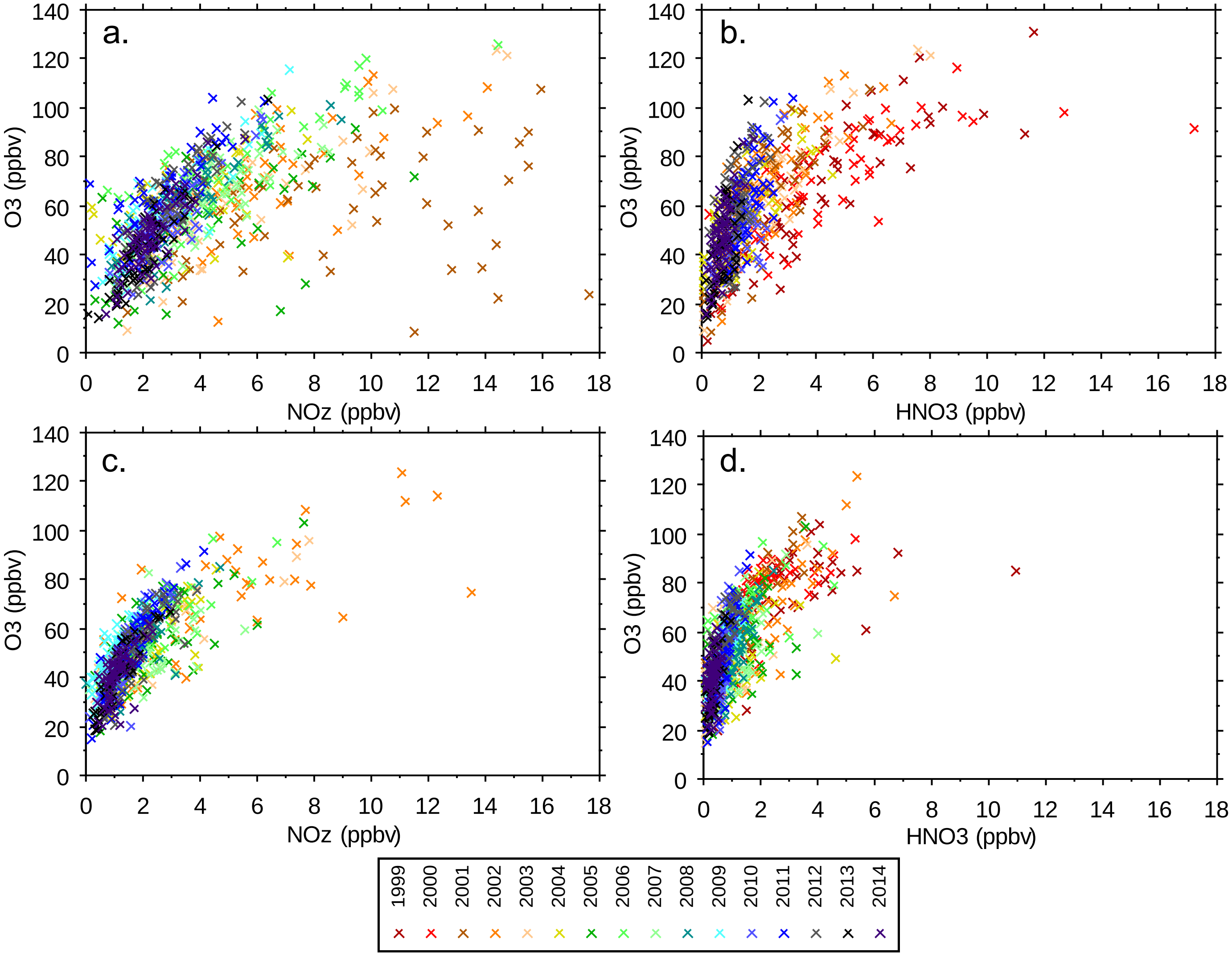
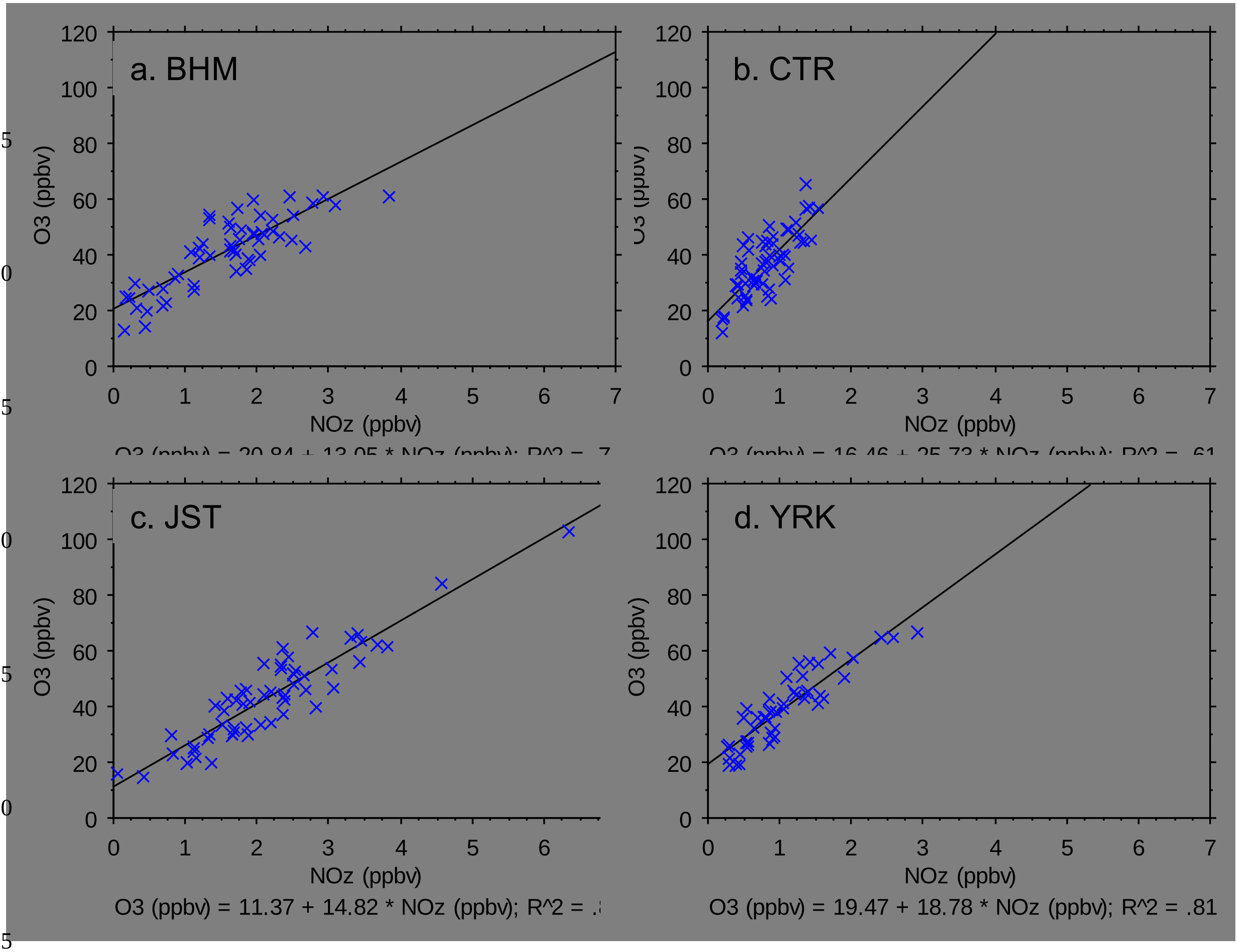


Figure 8. (a) O_3 vs. NO_z at JST; (b) O_3 vs. HNO_3 at JST; (c) O_3 vs. NO_z at YRK; and (d) O_3 vs. HNO_3 at YRK. Each point is the 2 – 3 p.m. hourly average on one day, limited to days in June or July and delineated by year. The 2001 and 2002 NO_z data may be biased high due to lower NO_2 mixing ratios obtained by the instrumentation used at that time (Figure S2).


a. BHM
b. CTR
c. JST
d. YRK
O3 (ppbv)
NOz (ppbv)
0
20
40
60
80
100
120
0
1
2
3
4
5
6
7
O3 (ppbv) = 20.84 + 13.05 * NOz (ppbv); R^2 = .7
O3 (ppbv) = 16.46 + 25.73 * NOz (ppbv); R^2 = .61
O3 (ppbv) = 11.37 + 14.82 * NOz (ppbv); R^2 = .
O3 (ppbv) = 19.47 + 18.78 * NOz (ppbv); R^2 = .81

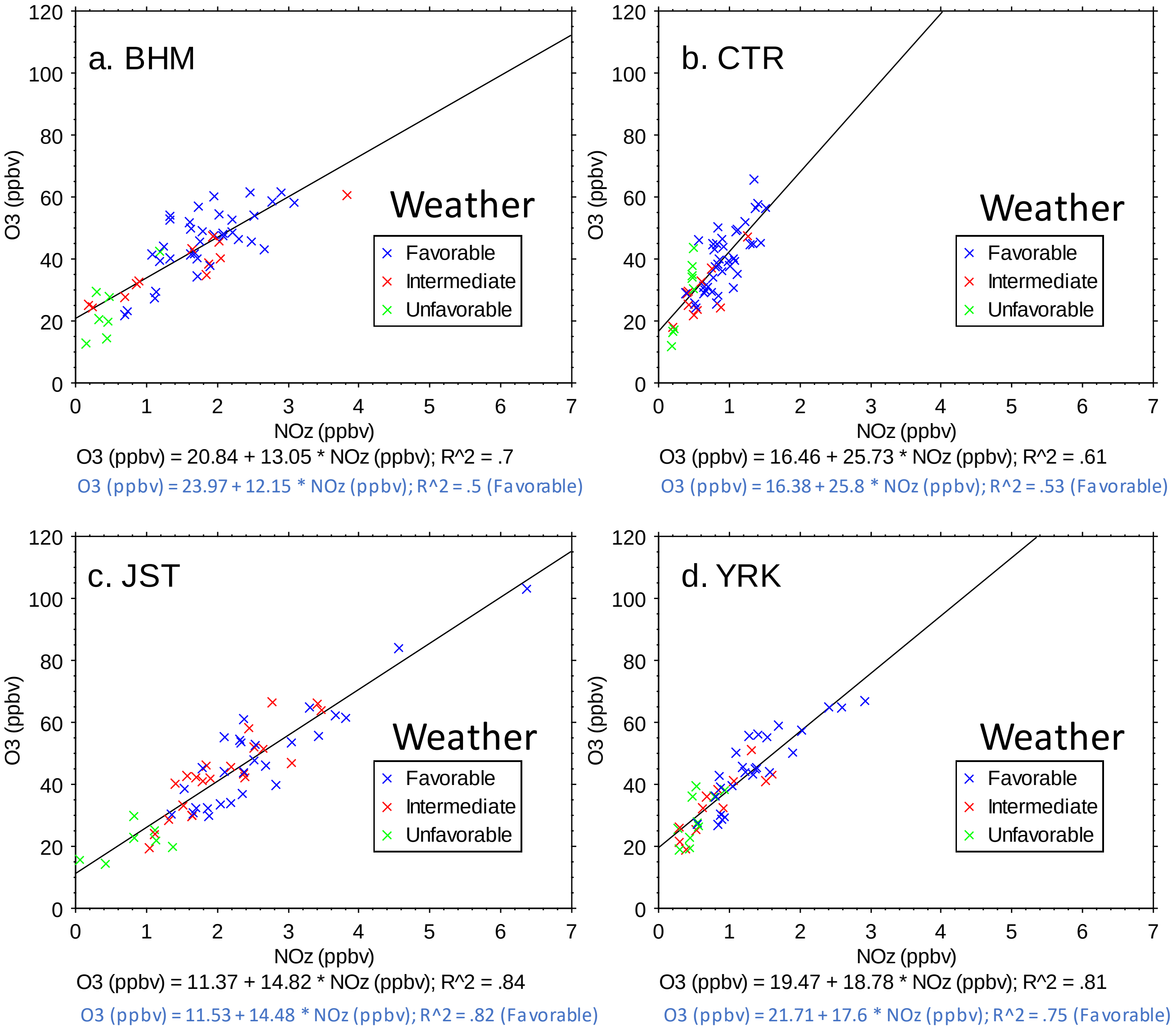


Figure 9. O$_3$ vs. NO$_z$ during June and July, 2013. Each point is the 2 – 3 p.m. hourly average on one day. The data were selected to represent the approximate mid-point of the mid-day O$_3$ maxima and to span a period around the summer solstice (- ~20 days, + ~40 days) when solar radiation is highest on average. The regression slopes ~~are interpreted as an indicator of observed OPE, and~~ show higher rural than urban values: BHM = 13.05 ± 1.19 ppbv ppbv^{-1}, JST = 14.82 ± 0.88 ppbv ppbv^{-1}, YRK = 18.78 ± 1.38 ppbv ppbv^{-1}, CTR = 25.73 ± 2.76 ppbv ppbv^{-1}. Corresponding regression slopes for O$_x$ vs. NO$_z$ are: BHM = 12.00 ± 1.16 ppbv ppbv^{-1}, JST = 13.88 ± 0.93 ppbv ppbv^{-1}, YRK = 18.85 ± 1.37 ppbv ppbv^{-1}, CTR = 25.79 ± 2.79 ppbv ppbv^{-1}. Symbols indicate the favorability of weather to O$_3$ formation and accumulation: (1) favorable = T > 25°C, RH < 70%, and solar radiation > 500 W m^{-2}, (2) intermediate = neither favorable nor unfavorable, (3) unfavorable = T < 25°C, RH > 70%, and solar radiation < 500 W m^{-2}. Regression results are shown for all days and for the days with favorable weather.

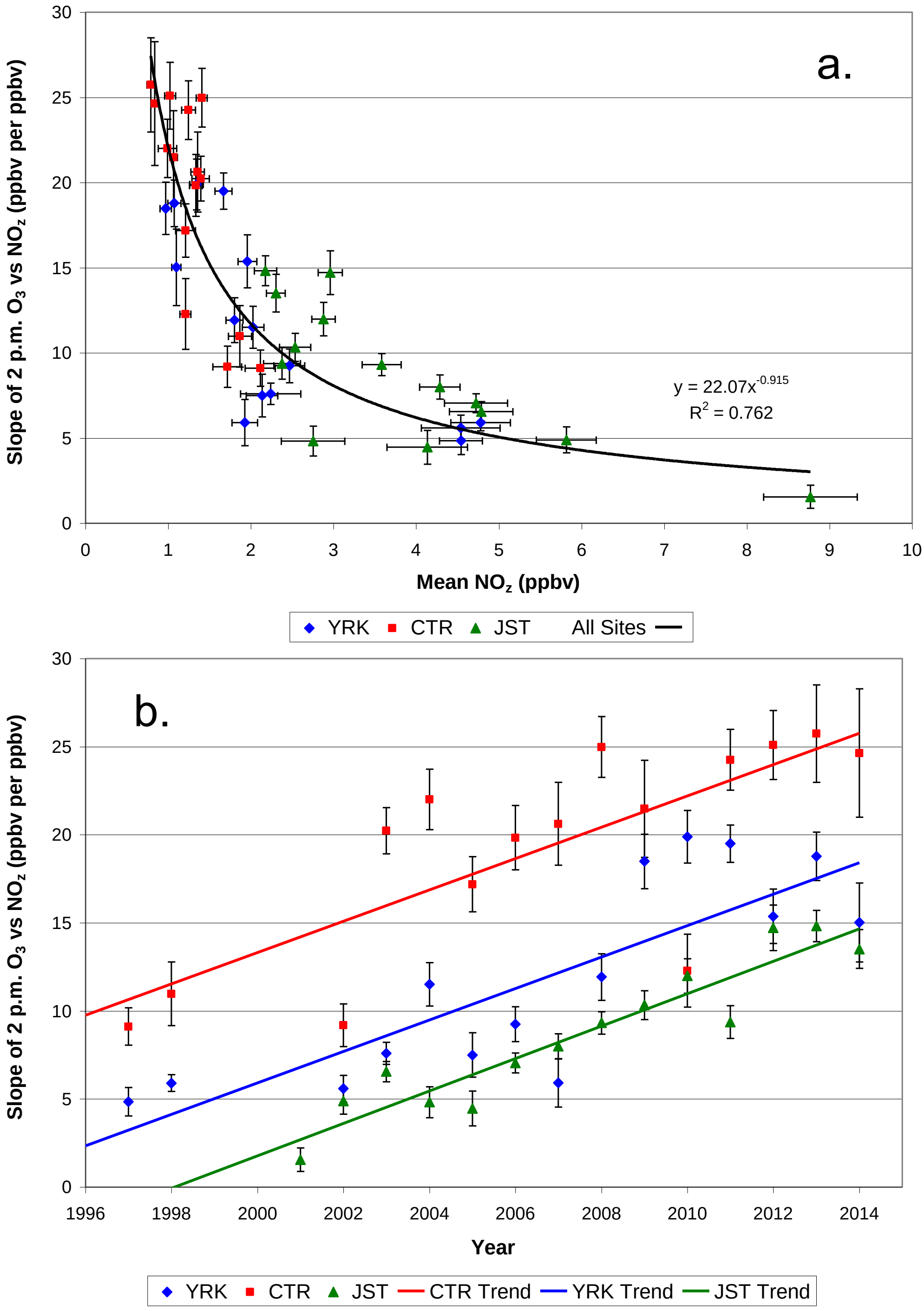


Figure 10. (a) Summer ~~observed OPE at~~ CTR, JST, and YRK ~~computed as~~ slope of daily (2 p.m.) O_3 and NO_z vs. mean (2 p.m.) NO_z mixing ratios, and (b) summer ~~observed OPE~~regression slope vs. year. NO_2 data were not available for 1999 through 2001. Vertical and horizontal error bars are one standard error of the regression slopes and one standard error of the NO_z means, respectively. Mean NO_z measurement uncertainty is estimated as 0.2 ppbv (1 sigma).