Response to Reviewer 1

We thank the reviewer for their helpful comments.

This manuscript is well-written, within the scope of ACP, and provides valuable evidence for the increasing importance of emissions of NO_x *from soils to ozone production as temperatures increase. This manuscript should be published after minor revisions detailed below.*

General Comments

1. The finding of increased soil NO_x *emission with temperature is valuable, and could be strengthened by a discussion of any known limitations on this effect, such as soil moisture or nitrogen availability. The authors discuss this briefly on page 12, but a more thorough discussion of what is known about microbes would be a valuable addition to this manuscript.*

We have expanded the discussion in our paper to discuss additional factors that affect soil NO_x emissions, including moisture, nitrogen availability, soil type, and pH:

" The only plausible source of NO_x that matches all of these constraints is soil microbial emissions near to the SOAS site. Soil NO_x emissions also depend on the water content and nitrogen availability, neither of which is generally limiting in the southeastern United States (e.g., Hickman et al., 2010)."

"Besides temperature, the most important variables affecting soil NO_x emissions are typically nitrogen availability and soil water content, as well as plant cover and soil pH (Pilegaard, 2013). In very wet environments, soil microbes typically emit N_2O or N_2 instead of NO_x, and in arid environments soil emissions of HONO can be equal to or larger than soil NO_x emissions (Oswald et al., 2013). Although conditions at the CTR site are too wet and acidic for soil HONO emissions to be significant, in environments where soil HONO emissions are large, they would likely have an even greater effect on ozone production by acting as a source of both NO_x and HO_x radicals.

The variability between sites and the interaction between several biotic and abiotic factors make it difficult to apply regional or model estimates of soil NO_x emissions to a particular location. Our approach from this study, using observations of the nighttime atmosphere to determine the NO_x emissions rate, helps span the gap between soil chambers and the regional atmosphere. Although soil NO_x emissions depend on several environmental factors, process-driven models predict that the response of soil NO_x emissions to global warming will be driven primarily by the increase in temperature (Kesik et al., 2006)."

2. The authors should improve the discussion of the effects of local meteorology on surface ozone. Jacob and Winner (2009) also discusses the strong positive relation- ship of ozone with temperature due to the association of temperature with regional stagnation. Was there stagnation on warmer days that would be a contributing factor to the ozone-temperature relationship? Convince the reader of the extent of the effect of the increased NO_x *emissions on this relationship in the context of likely different meteorology on hot days.*

Fully disentangling the effects of meteorology, chemistry, and emissions on surface ozone is an open problem, and one that is difficult to answer with in-situ measurements. We have added greater discussion of the possible effects of stagnation on ozone, as well as an indirect calculation of the contribution of non-chemical effects to the ozone temperature-relationship by comparing how the chemical production, chemical loss, and concentration of ozone all vary during SOAS:

"Regional stagnation episodes, often associated with elevated temperatures, allow ozone to accumulate over several days and are known to contribute significantly to the ozone-temperature relationship (Jacob et al., 1993). How various temperature-dependent chemical effects interact and their relative contributions to ozone production are not well understood outside of polluted environments. "

"While elevated temperatures are associated with enhanced production of ozone, they are also associated with increased chemical loss. The chemical loss of ozone occurs through three main pathways in this region: photolysis followed by reaction with H_2O, reaction with HO_2, and reaction with VOCs (Frost et al., 1998). The loss of O_3 was calculated for each of these pathways, and then integrated over the course of the day to determine total daily ozone loss ($\int LO_3$). Chemical loss of ozone is found to increase with temperature (1.1 ± 0.3 ppb $^\circ C^{-1}$, Fig. 3b), but much less than the chemical production.

The difference between the trend in the net chemical production and loss of O_3 and the trend in ozone concentration gives a rough estimate of how non-chemical processes contribute to the ozone-temperature relationship. We calculate that non-chemical processes cause O_3 to increase by 1 ± 1.2 ppb $^\circ C^{-1}$. This approach does not take into account the interactions between chemical and non-chemical effects, such as how changes to advection and mixing may impact concentrations of VOCs, NO_x, and other reactants. Although the large uncertainty does not allow for quantitative analysis, qualitatively, chemical and non-chemical processes are both found to be important contributors to the ozone-temperature relationship. Other approaches, such as chemical transport models, that can more directly investigate and control specific physical processes are likely to be better suited to calculating the contribution of non-chemical processes to the ozone-temperature relationship (e.g., Fu et al., 2015). "

3. A final valuable addition would be a statement about whether the authors observe any breakdown of the observed ozone-T relationship at the highest temperatures, as found by Shen et al, 2016 (GRL), or whether their approach could be applied to this problem as well or would be impacted by this phenomenon.

We thank the reviewer for bringing this phenomenon to our attention. Following Shen et al., 2016, we have examined the relationship between ozone and temperature, as well as between ozone production and temperature, in the 5% hottest days from June-August 2010-2014. We find no significant differences between the trend in the top 5% of temperatures and the bottom 95% percent. We have revised the paper to include a mention of this phenomenon, and the results from our analysis:

"A few studies have also reported that this effect is non-linear and can become significantly less strong at the highest temperatures (Steiner et al., 2010; Shen et al., 2016)."

"Based on the long-term SEARCH record, we do not find evidence that the relationship between ozone concentration or ozone production changes significantly at the highest temperatures (the top 5% of observations). This agrees broadly with Shen et al. (2016), who found that ozone suppression at extreme temperatures to be uncommon in the southeastern United States. "

Page 2, line 17-18 – Could you clarify the point of Berlin et al, 2013? They are talking about 'background' ozone coming in to Houston, and I don't see the connection between your point about rural ozone and this paper.

The analysis of Berlin et al., 2013 is indeed about regional background ozone coming in to Houston. When air is entering Houston from the north or northeast, this regional background will contain a component of ozone from rural areas and is associated with greater probability of regulatory exceedances in the Houston area. We have revised this sentence to more accurately reflect the results of Berlin et al., 2013:

"From a regulatory perspective, elevated regional background ozone can strongly exacerbate ozone pollution and the probability of regulatory exceedances in urban areas such as Houston (Berlin et al., 2013). "

Page 4, line 23-24 – You say, "When HNO_3 is the most important NO_x loss pathway, O_3 production and NO_x loss occur through separate channels and can change independently." Can you clarify this? Aren't both pathways competing for NO_2, so they are not actually independent? In the example that follows, more explicit statements of what is happening would be useful.

We have revised this section emphasize our point that the relative importance of these two channels can vary, rather than that ozone production and NO_x loss are strictly independent:

" As the concentration of NO_x decreases and VOCR increases, the fraction of NO_x loss that takes place via HNO_3 chemistry decreases and the OPE increases (Fig. 2c). The relative importance of HNO_3 and $RONO_2$ chemistry determines the relationship between PO_3 and LNO_x. When HNO_3 is the most important NO_x loss pathway, O_3 production and NO_x loss occur through separate channels. O_3 production occurs when OH reacts with a VOC, generating RO_2 and HO_2 radicals; NO_x loss primarily occurs when OH reacts with NO_2. Although these channels are linked by a shared dependence on OH, the relative importance of these pathways can vary. For example, under these conditions an increase in VOCR will cause NO_x loss to decrease, ozone production to increase, and OPE to increase (Fig. 2b–c).

In contrast, when $RONO_2$ chemistry dominates NO_x loss, ozone production and NO_x loss are intrinsically linked by their shared dependence on the RO_2 + NO reaction. This reaction produces O_3 in its main channel and consumes NO_x in the minor channel that forms organic nitrates, with the ratio between these two channels set by α_{eff}. Under these conditions, changes to the chemistry that do not affect α_{eff} have a minimal effect on OPE (Fig. 2d) and the OPE can be considered to be unvarying with temperature. An increase in VOCR or a decrease in NO_x will affect both NO_x loss and ozone production equally, because both processes are dependent on the same set of reactions. Because of this change in behavior, from variable OPE to fixed OPE, the drivers of the O_3-T relationship are expected to be categorically different in areas where $RONO_2$ chemistry dominates NO_x loss. As a result, the effects that cause O_3 to increase with temperature in urban and other polluted regions, where HNO_3 chemistry dominates NO_x loss, are unlikely to apply in areas with low concentrations of NO_x and high concentrations of reactive VOCs, where $RONO_2$ chemistry is most important. In these areas, more NO_x must be oxidized in order to produce more O_3. "

Page 4, line 30 – It is unclear to me whether you include thermal decomposition of PAN for example here, so that if temperature goes up, the effective yield of the sink would go down and OPE would not be fixed.

We do not include PAN in these calculations. PAN is quite short lived under typical conditions of the CTR site, and therefore does not serve as a permanent sink of NO_x. Furthermore, it has been found at multiple forested locations that total peroxy nitrate concentrations do not vary significantly with temperature, due to changes in both production and loss. As a result, the effect of PAN on OPE is likely to be small. We have added a paragraph to section 2 explaining this reasoning:

" NO_x also has several temporary sinks that can sequester NO_x, most importantly peroxy acyl nitrate (PAN). In the summer-time southeastern United States, the lifetime of PAN is typically 1–2 hours, too short to act as a permanent sink of NO_x. Past studies in forested regions have found remarkably little variation in PAN with temperature, due to compensating changes in both its production and loss (e.g., LaFranchi et al., 2009). As a result, the formation or destruction of PAN does not contribute significantly to net ozone production or NO_x loss and we do not include it in these calculations. "

Also, if you are integrating over a day, do you think that ignoring deposition is at all important?

Since deposition of NO_x is far slower than its chemical removal, deposition will only affect OPE if it affects the fraction of NO_x sinks that recycle or remove NO_x from the atmosphere. Deposition is not a major sink for any of the species that can recycle NO_x to the atmosphere and therefore changes in deposition with temperature are unlikely to be important. We have expanded our discussion of $RONO_2$ chemistry to explain this effect:

"Deposition is only a minor loss process for $\Sigma RONO_2$, therefore any changes in the deposition rate with temperature will have at most a minor effect on η. "

Page 7, line 18 – How does an average OPE of 45 compare to OPE calculated from your model of PO_3/LNO_x?

To better constrain our understanding of OPE, we compare the OPE calculated from the ratio of $\int PO_3$ and $\int LNO_x$ to the OPE calculated as the ratio of O_x to NO_z. These two different calculations of OPE agree reasonably well, bolstering our confidence in the calculated ozone production and NO_x loss rates:

" OPE can also be estimated from the ratio of odd oxygen ($O_x \equiv O_3 + NO_2$) to NO_x oxidation products ($NO_z \equiv NO_y - NO_x$) (Trainer et al., 1993). The afternoon ratio of O_x to NO_z during SOAS varied from 43–67 (interquartile range), slightly higher than the average ratio of $\int PO_3$ to $\int LNO_x$. However, since the O_x to NO_z ratio includes the effects of chemical loss and transport, which the ratio of $\int PO_3$ to $\int LNO_x$ does not, these two values are not expected to be equivalent, particularly in non-polluted areas. "

Page 7, line 19 – Why do you say there is no OPE trend, but then provide a value (0.2)? If it is not statistically significant, don't show a number.

We think that the calculated trend and error in OPE with temperature provide useful information even though the trend is not statistically significant. Because both the calculated trend and error are close to zero, we can be confident that OPE does not change dramatically with temperature, even though the trend is not significantly different from zero. We have revised this sentence to emphasize the result that OPE is found not to vary with temperature rather than the statistical significance of the result:

"As expected from the importance of $RONO_2$ chemistry to NO_x loss, $\int LNO_x$ and $\int PO_3$ are tightly correlated ($r^2 = 0.90$), and OPE is high (OPE average 45±3 ppb ppb^{-1}) and is effectively constant with temperature (calculated trend $0.2 \pm 0.6\ ^{\circ}C^{-1}$). Therefore, the increase in $\int PO_3$ with temperature is not caused by more efficient production of ozone while the same amount of NO_x is consumed."

Page 10, line 20 – You say, "The increase of PHO_x is mostly driven by increased solar radiation, and not by temperature directly." Could it not also be driven by increased water vapor with higher temperatures?

While water vapor is a major reactant in HO_x radical production, we find that its contribution to the increase of PHO_x with temperature to be minimal at this location. Water vapor is effectively constant with temperature and is not correlated with the total PHO_x rate, while solar radiation increases with temperature and is well correlated with the total PHO_x rate. Because of this difference, we are confident in assigning the change in PHO_x to variation in solar radiation. We have expanded the discussion of PHO_x and added a figure to the supporting information to clarify our reasoning:

"The increase in $P\mathrm{HO_x}$ with temperature is most likely caused by changes in solar radiation, which is well correlated with the total $P\mathrm{HO_x}$ rate (Fig. S7a) and increases strongly with temperature. In contrast, water vapor is not correlated with total $P\mathrm{HO_x}$ (Fig. S7b). "

Page 12, line 22 – You say "These emissions cannot be regulated or controlled directly, and therefore present challenges to traditional air quality management techniques." Then this statement seems to be a contradiction - "Alternative approaches, such as changes to fertilizer application practices, have the potential to significantly reduce SNOx from agricultural regions (Oikawa et al., 2015)."

We have removed the statement that soil NO_x emissions cannot be regulated or controlled directly, and instead emphasize that there are additional difficulties associated with controlling sources of NO_x distributed over large areas:

"Because these emissions are distributed over broad areas and are not directly anthropogenic, they present additional challenges to air quality management. Indirect approaches, such as changes to fertilizer application practices, have the potential to significantly reduce $S_{\mathrm{NO_x}}$ from agricultural regions (Oikawa et al., 2015). "