

# Response to interactive comment on “Atmospheric oxidation of isoprene and 1,3-butadiene: influence of aerosol acidity and relative humidity on secondary organic aerosol” by M. Lewandowski, M. Jaoui, J.H. Offenberg, J.D. Krug, and T.E. Kleindienst

**Commentator A. Nenes**

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The interpretation of the experimental results relies heavily on the ability of  $[H^+]_{air}$  to capture the in-situ pH of atmospheric particles. The methodology of Surrat et al. (2007) involves extracting filter samples in water, measuring its pH and then back-calculating the amount of  $H^+$  in the original aerosol (assuming that  $H^+$  is conserved). This is largely equivalent to an “ion balance” method, because the  $H^+$  measured corresponds to an aerosol sample diluted by orders of magnitude, so that the ions present are largely dissociated (this is affected by the degree of dilution used, but does not change the inherent nature of the methodology). However, two studies currently in discussion in ACPD (Guo et al., 2014; Hennigan et al., 2014) raise doubts on whether such methods can be used as a proxy for in-situ aerosol pH, as it is shown that  $H^+$  from ion balance is not correlated with in-situ aerosol pH for a wide range of aerosol conditions. This is especially relevant for this study as chamber RH is varied; the latter affects the amount of in-situ aerosol liquid water (hence pH) in a way that is not reflected in  $[H^+]_{air}$ . Even if a constant RH were used as in Surrat et al. (2007), the variable chemical composition (and potentially phase state) of the particles across experiments can still have a nontrivial effect on aerosol liquid water content, hence in-situ pH.

With the above said, we are not implying that the study here is fundamentally flawed. However, it would be good to see the acidity interpretation accompanied by both  $[H^+]_{air}$  and pH calculations from a thermodynamic model (e.g., AIM, ISORROPIA, MESA) applied to the chamber conditions. Guo et al. (2014) and Hennigan et al. (2014) have shown that models applied to complex SE US and Mexico City aerosol, even at relatively low RH, can provide a much better representation of aerosol pH than ion-balance methods, provided that they are applied in “forward mode”. This is what we recommend here as well to be done. In the absence of gas-phase inorganic component measurements, one can still apply thermodynamic models in a useful manner (e.g., Guo et al., 2014).

We generally agree with the reviewer’s assessment of the limitations of the  $[H^+]_{air}$  measurement. Although we believe that the limitations inherent in the measurement may not be as pronounced under the controlled conditions of a laboratory experiment as they are under ambient sampling conditions, it remains at best an indirect measurement of the aerosol properties of interest. We have retained the  $[H^+]_{air}$  metric in the early part of the paper's results (isoprene/ $SO_2$  and 1,3-butadiene vs  $[H^+]_{air}$ ) in part for consistency with previous studies, especially the isoprene/ $SO_2$  comparison to Surratt et al 2007. While these experiments could certainly benefit from additional information regarding the actual aerosol pH levels, we do not believe that this information is vital to the comparisons presented.

In the varied RH experiments, where  $[H^+]_{air}$  measurements are of limited value (since the maximum dissociated  $H^+$  in the extracts remains unchanged, but actual aerosol pH is expected to change with liquid water content), we agree with the reviewer that aerosol pH levels or aerosol liquid water concentrations would be of tremendous value to the interpretation of the results. Unfortunately, we do not have sufficient composition information to do the modeling with ISORROPIA or AIM appropriately. While chamber temperature, RH, and particle sulfate loading are known for each reaction step, particle phase ammonium and nitrate were not

measured in these experiments. And, although not strictly necessary, no gas-phase ammonia or nitric acid concentrations are available (and, as high-NO<sub>x</sub> experiments, nitric acid concentrations should be non-trivial), further complicating model predictions. Additionally, as with the SOAS field measurements reported in Guo et al (2014), we have a significant aerosol fraction composed of isoprene-related organic aerosol to contend with, which can further contribute to aerosol phase water content, but is not accounted for in the models.

Given these limitations, we believe that any modeled pH levels or aerosol liquid water concentrations that we could generate from our existing data would be suspect and potentially counterproductive to the analysis (due more to our under-analysis of the aerosol composition than to any limitations inherent in the models). While we readily admit that humidity provides, at best, an indirect measure of the physically important aerosol parameters of interest in these comparisons, it is nevertheless the most reliable measurement surrogate that we have to work with in this data set. As such, we have retained it in the comparisons, but have added additional text to the Methods section further clarifying the limitations of both  $[H^+]_{air}$  measurement in lieu of aerosol pH, and the use of humidity level as a surrogate for aerosol liquid water content (Line 165):

“While this method provides a simple, easily repeatable measure of bulk acidity, it does not fully capture the actual acidity of individual aerosol particles, which is more likely to be of physical significance in these chemical systems. It is also of limited value in experiments where the relative humidity is varied, as the extraction of the collected aerosol effectively masks the effects of changing particulate liquid water concentrations. Further limitations of the  $[H^+]_{air}$  measurement techniques have been described in detail in Hennigan et al. (2014). While a number of methods have been developed to measure aerosol liquid water content directly or estimate it through the use of thermodynamic models such as ISORROPIA (Fountoukis and Nenes, 2007) or AIM (Wexler and Clegg, 2002), liquid water measurements were not available for this study, and insufficient aerosol compositional information was collected for accurate use of thermodynamic modeling.”

We have also added a Summary section which includes an additional review of the limitations of the experiments presented in the paper, including areas requiring additional investigation in future work, which includes discussion of the need for aerosol liquid water or pH assessments in future work (line 470):

“While these experiments are suggestive, they also include a number of shortcomings that need to be addressed in future work. Perhaps the most significant is the use of absolute humidity and  $[H^+]_{air}$  as surrogate measures of aerosol liquid water content and aerosol pH. Determination of the effective pH in the aerosol particles through the application of thermodynamic models, such as ISORROPIA or AIM, should provide a more realistic assessment of actual acidity than the  $[H^+]_{air}$  approach, provided adequate gas and particle composition data is obtained experimentally. However, even these models generally account for only the influence of inorganic species, while the presence of isoprene SOA products has been reported to also contribute significantly to water uptake on ambient aerosols (Guo et al., 2014). This suggests that for laboratory experiments with high organic aerosol concentrations, particularly from isoprene-related parent hydrocarbons, direct measurements of aerosol liquid water content may be required.”

## Anonymous Referee #1

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Do the authors think that water vapour plays a role in the VOC oxidation chemistry leading to a lower SOC yield at an elevated humidity level or is it more related to particle phase chemistry such as a lower yield organosulfates, enhanced hydrolysis or reduced absorptive partitioning of organic compounds due to lower organic mass? Can the authors discuss this in the manuscript?

Given the relatively limited organic compositional analysis available in these experiments, it is difficult to assess the potential changes in VOC chemistry occurring as RH is varied. As no significant changes in NO<sub>x</sub> or ozone concentrations were observed, and that the delta hydrocarbon remained essentially constant at all RH levels, it would appear that at least the early generations of VOC oxidation chemistry remained essentially unchanged (in contrast, the changes in the yield of the SO<sub>2</sub> to sulfate reactions with changing RH did result in observable changes in NO<sub>x</sub>, O<sub>3</sub>, and delta SO<sub>2</sub> concentrations, although this data was not presented in detail in the paper). Reductions in the formation of oligomeric species or organosulfates in a more water-rich environment seem plausible, but we currently lack the detailed organic analyses needed to back up these ideas. Further experiments are pending on these topics. Additional discussion added to the manuscript at Line 371:

“The reason for this reduction in SOC formation is not entirely clear. Gas-phase NO<sub>x</sub> and O<sub>3</sub> concentrations do not appear to change significantly as a function of humidity level, as does the concentration of isoprene consumed in the reactions. This suggests that early-generation gas-phase oxidation reactions are probably not altered significantly by changing humidification. Changes in the aerosol liquid water content may affect the gas-particle partitioning of later-generation isoprene oxidation products, or increased water content may affect particle-phase organosulfate formation or the formation of oligomeric species (Pye et al., 2013). Further analysis of gas- and particle-phase organic constituents is required to further investigate this effect.”

Pp. 29441 Line 21 onwards: Is the sulfate acidity effect purely related to the reactivity of oxidation products to acidic sulfate? I imagine that the layer of SOA formed on the seed particle likely hinders acid catalysed accretion reactions and absorptive partitioning largely controls the subsequent SOA formation. In other words, VOCs with higher  $\Delta M_{SOA}$  may not show a strong acidity effect. How do the placements of these VOC relate to  $\Delta M_{SOA}$  from neutral seed experiments?

Although interface and/or transport effects may impose limits on acid catalyzed reactions at some concentration level, no clear indications were observed in these experiments. As noted in Section 3.1, variations in the particulate sulfate loading in the isoprene/SO<sub>2</sub> experiments (due to the concentration of SO<sub>2</sub> employed in different stages) produced linear OC vs [H<sup>+</sup>] behavior essentially identical to previous experiments conducted with constant sulfate concentrations generated with nebulized sulfate aerosol. In addition, Offenberg et al (2009) previously considered different organic loading with  $\alpha$ -pinene SOC with no obvious differences in the results. It is possible that the organic to sulfate ratios used in these experiments simply do not reach a critical threshold at which interface effects would become limiting. However, it is also possible that there are additional factors, such as aerosol phase and/or mixing state, which would negate the limiting interface conditions of the core/shell structure suggested by the reviewer. The need for further examination of the physical characteristics of the particle phase are now included in the Summary section (Line 486):

“Further examination of the mixing state and phase of the generated aerosols would also like be of value, given that the available interfacial area could affect interactions between H<sup>+</sup>, sulfate, and SOA, which may in turn affect organosulfate formation or other pathways to increased SOA yield.”

Pp. 29442 Line 19 onwards: Temperature data should be given in Tables 1 and 2. How large was the temperature differences between these experiments? If the temperature had a significant impact on the RH, it is likely that the temperature also had an influence on the  $\Delta M_{SOA}$ . Can the authors discuss about this in the manuscript?

The referenced text applies to the relative humidity variation experiments, which are detailed in Figure 4 (not Figures 1 and 2). Figure 4 has been modified to include temperature and relative humidity ranges for the described experiments, in addition to the absolute humidity ranges already provided.

Pp. 29442 Line 25 and Pp. 29443 Line 21 onwards: There are several thermodynamic models available to calculate aerosol water content and pH values. The authors may want to use one of these tools to estimate the values for these experiments and add them to Tables 1 and 2, and discuss if these parameters had an influence on acid catalysed accretion reactions or not.

See response to comments from A. Nenes, above.

Pp. 29444 Line 27: I would like the authors to discuss a bit deeper about the structural differences of oxidation products here. What sort of oxidation products do the authors expect when there is an additional methyl group in a precursor VOC? Does this lead to more reactive intermediate oxidation products towards acidic sulfate?

Given the current length of the paper, and the additional analytical techniques (GC-MS and/or LC-MS) that would need to be incorporated in order to provide a detailed discussion of the organic compositions of the isoprene and 1,3-butadiene systems, we have chosen to not include a more detailed discussion of the oxidation products here. We have instead qualified that this proposed pathway is speculative at this time, included a recent reference to 1,3-butadiene reaction mechanisms in general, and have suggested that this topic will need further discussion in a future manuscript. See Line 334 in Results and Discussion:

“This could represent a substituent effect which influences the sensitivity of the gas-phase precursors to reaction by the acidic sulfate nucleophile, but further organic analysis of the aerosol phase constituents would be required to examine this possibility in detail. Although recent studies have compared the reaction pathways and products formed for 1,3-butadiene oxidation versus isoprene oxidation (Jaoui et al., 2014), these studies did not focus on acid-influenced reactions or organosulfate formation.”

and line 493 in the Summary:

“A further examination of the similarities and differences between acid-influenced OC formation in the isoprene and 1,3-butadiene systems would also likely be valuable. A more rigorous organic analysis of product distributions may help reveal why isoprene appears to be significantly more sensitive to acidic conditions than 1,3-butadiene at low humidity levels, and whether this difference is due to structural effects related to the additional methyl group affecting gas-phase chemistry, particle-phase organosulfate formation, or due to other phenomena, such as differences in volatility and partitioning

of oxidized intermediates. A more detailed comparison of isoprene and 1,3-butadiene organic chemistry under acidic conditions may help with the development of more accurate mechanisms for inclusion in air quality models.”

As other reviewer commented, the authors should discuss their findings in atmospheric relevant context at the end of the manuscript.

A Summary section has been added to the paper, which incorporates a discussion of the relevance of these studies to atmospheric conditions, as well as a thorough assessment of the current limitations of the experiments presented (Lines 445-469):

“These experiments support previous studies suggesting that acidic aerosol can lead to increased SOA formation from the photooxidation of isoprene under laboratory conditions. Changing the source of the acidity from nebulized inorganic aerosol to a more atmospherically relevant photochemical conversion of SO<sub>2</sub> into acidic sulfate aerosol nearly identical results as previous nebulized sulfate aerosol experiments. In addition, 1,3-butadiene, a chemically similar compound released from primarily anthropogenic sources, was also demonstrated to produce higher concentrations of SOA under acidic conditions, albeit to a lesser extent than was seen with isoprene. The humidity experiments further suggest that aerosol liquid water content can have a substantial effect on SOA formation from isoprene and 1,3-butadiene. Increasing humidity produces a notable reduction in SOC formation in both the isoprene and 1,3-butadiene photochemical systems, which is more pronounced in both systems in the presence of acidic inorganic aerosols, and was most pronounced for the acidified isoprene/NO system.

In the isoprene/NO photochemical systems examined in this study, SOC enhancement due to the presence of acidic inorganic aerosol was observed to be negligible at absolute humidity levels above approximately 11 g H<sub>2</sub>O m<sup>-3</sup>. This lower SOC enhancement at elevated humidities may explain, in part, the difficulties in detecting increased SOA formation under acidic conditions in field studies of ambient air masses, particularly in humid climates like the southeastern US. This work suggests that a more detailed understanding of the role of humidity and of aerosol liquid water content is likely required in order to accurately predict the impact of acidity-influenced oxidation chemistry on overall SOA yields. While the data presented here may suggest that enhanced SOA formation via acid-influenced pathways is more constrained than previous studies may have suggested, it does still appear to represent a viable pathway for additional SOA formation from a number of precursor hydrocarbons, which may need to be incorporated into air quality models in order to accurately estimate secondary PM concentrations in certain locations.

While these experiments are suggestive, they also include a number of shortcomings that need to be addressed in future work. Perhaps the most significant is the use of absolute humidity and [H<sup>+</sup>]<sub>air</sub> as surrogate measures of aerosol liquid water content and aerosol pH. Determination of the effective pH in the aerosol particles through the application of thermodynamic models, such as ISORROPIA or AIM, should provide a more realistic assessment of actual acidity than the [H<sup>+</sup>]<sub>air</sub> approach, provided adequate gas and particle composition data is obtained experimentally. However, even these models generally account for only the influence of inorganic species, while the presence of isoprene SOA products has been reported to also contribute significantly to water uptake on ambient aerosols (Guo et al., 2014). This suggests that for laboratory

experiments with high organic aerosol concentrations, particularly from isoprene-related parent hydrocarbons, direct measurements of aerosol liquid water content may be required.

Additionally, the relative humidity experiments presented here consider predominantly systematic increases in relative humidity. As some phenomena related to aerosol liquid water content are known to display hysteresis, such as deliquescence of sulfate aerosols, further testing. Experiments incorporating descending relative humidities and larger humidity steps are warranted, particularly along with the inclusion of liquid water content measurements. Further examination of the mixing state and phase of the generated aerosols would also like be of value, given that the available interfacial area could affect interactions between  $H^+$ , sulfate, and SOA, which may in turn affect organosulfate formation or other pathways to increased SOA yield.

Finally, further research is needed to examine changes in organic composition triggered by the effects considered in this work. In particular, the mechanism through which humidity level affects OC production from isoprene, even under non-acidified conditions, could be important to the selection of appropriate SOC yields in air quality models. A further examination of the similarities and differences between acid-influenced OC formation in the isoprene and 1,3-butadiene systems would also likely be valuable. A more rigorous organic analysis of product distributions may help reveal why isoprene appears to be significantly more sensitive to acidic conditions than 1,3-butadiene at low humidity levels, and whether this difference is due to structural effects related to the additional methyl group affecting gas-phase chemistry, particle-phase organosulfate formation, or due to other phenomena, such as differences in volatility and partitioning of oxidized intermediates. A more detailed comparison of isoprene and 1,3-butadiene organic chemistry under acidic conditional may help with the development of more accurate mechanisms for inclusion in air quality models.”

Pp. 29432 Line 2 and elsewhere: I feel that  $[H_3O^+]_{seed}$  or  $[H_3O^+]_{aerosol}$  is more appropriate for expressing the aerosol acidity. It is very unlikely that free  $H^+$  exists in the air under the experimental conditions used by the authors.

Although we agree that the  $[H^+]_{air}$  terminology, generally defined as the dissociable  $H^+$  in the aerosol per cubic meter of air sampled, can be misleading and subject to misinterpretation, it does have prior established use in the literature. In order to maintain consistency with these prior publications, the terminology has been retained here.

## Anonymous Referee #2

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1) A major point of concern in this manuscript, as identified by the authors and further detailed in the short comment by A. Nenes, is the measurement of  $[H^+]$  and its relationship with particle acidity and relative humidity. While the method used provides a valid bulk measurement, it is not clear whether bulk  $[H^+]$  is particularly atmospherically relevant when other factors (e.g. particle water content) can influence acidity. In light of these concerns, I would suggest that the authors find addition methods, such as calculating particle acidity with a thermodynamic model, for approaching this intractable issue. As A. Nenes describes, such models have been shown to give reasonable estimates of aerosol pH, and when used in conjunction with measured bulk  $[H^+]$ , these estimates will provide a clearer interpretation of acidity in the particle phase. Of particular concern, in light of the difficulty of measuring particle acidity, are experiments in which multiple factors influencing acidity change together, such as the relative humidity experiments detailed in this manuscript. For reasons discussed in the manuscript, it can be hard to know how much the change in SOC yield reflects variations in humidity directly, or indirectly by changes in particle acidity, which may be changing despite a constant  $[H^+]$  due to differences in particle water content. Employing thermodynamic models to estimate particle pH would be particularly useful for these experiments.

[See response to comments from A. Nenes, above.](#)

Additionally, considering the difficulty of separating the effects of humidity and acidity in these experiments, discussion of further controls would be beneficial in Section 3.3. For example, the authors mention temperature differences between experiments (L320); could these temperature differences also have an effect on SOC yields? Also, when the relative humidity was stepped up and down in these experiments, could hysteresis effects influence SOC yield, by which particles formed at one humidity and then brought to another humidity have different organic content than particles formed at the second humidity level (e.g. by irreversible particle-phase reactions)? A discussion of these temperature and hysteresis effects, and particularly any control experiments run to investigate these effects, would provide valuable insight into the many factors at play in these humidity experiments.

[Although it is difficult to say with certainty how strongly the SOC yields may be impacted by temperature variations, we believe that the effects should be relatively small in the directly compared data sets presented in the paper. In the 1,3-butadiene/humidity experiments, the temperature differences between the two runs are approximately 3°C, with the seed experiment having the higher temperature. In the isoprene/humidity experiments, the overall temperatures were higher than the 1,3-butadiene experiments \(by approximately 2 and 5 degrees C\), but consistent with one another to within about 1°C. This may account for some of the differences in the observed behavior of the two systems, such as the greater separation of the butadiene curves at elevated humidity levels, but other sources of experimental error are likely to have a greater overall effect \(as suggested by the scatter in the OC and yield plots\) than the temperature differences. However, since converting from relative to absolute humidity could correct for the roughly 10-15% difference in water concentrations produced by these temperature differences, we felt that incorporating this correction improve the comparability of the datasets. We have adjusted the text to more directly provide the temperatures at which the different experiments have been conducted \(in various locations\), and have included an explicit mention of the possibility of temperature differences affecting the 1,3-butadiene RH experiments \(Line 436\):](#)

“Additionally, the temperature difference between the two experiments, although relatively small (approximately 3 °C on average) may be sufficient to introduce differences in the gas-particle partitioning between the two experiments.”

With regards to hysteresis effect, in all described experiments the chamber system was allowed to equilibrate for at least 4 residence times following any change to the reaction conditions. This should allow for near-complete (>95%) turnover of all products formed under the previous conditions, which should minimize or eliminate any hysteresis effects from the causes suggested by the reviewer. However, other sources of hysteresis, such as deliquescence behavior of the inorganic sulfate, are more difficult to rule out. A limited number of additional data points were collected to attempt to test for hysteresis due to the direction or magnitude of the RH changes. However, due to the challenges of these long-running experiments, not enough data was obtained to produce a statistically significant assessment. Text has been added to the Summary section identifying this as an outstanding experimental issue warranting further study (Line 482):

“Additionally, the relative humidity experiments presented here consider predominantly systematic increases in relative humidity. As some phenomena related to aerosol liquid water content are known to display hysteresis, such as deliquescence of sulfate aerosols, further testing. Experiments incorporating descending relative humidities and larger humidity steps are warranted, particularly along with the inclusion of liquid water content measurements.”

2) Some discussion is needed at the end of the manuscript about the atmospheric relevance and implications of the results. Do these experiments provide any insight into field observations, and their persistent disparities from chamber experiments regarding the dependence of SOC yield on particle acidity? What effects might these humidity and acidity dependencies have on particle SOC yields in atmospheric conditions where isoprene and 1,3-butadiene are found?

A Summary section has been added to better summarize outstanding experimental issues related to this study and potential atmospheric implications for ambient SOA formation, particularly for isoprene (Lines 445-469). The text is provided above in the response to Reviewer #1.

3) Minor clarification questions about methods and instrumentation:

L151 – In the discussion of measuring  $[H^+]$ , some detail on the subject of uncertainty (e.g. the error bars shown on Figures 1, 2, 3, and 5) would be useful. How are these errors estimated, and what factors are (and are not) included?

L165 – A similar treatment of uncertainty in the discussion of particle organic carbon measurements would be useful as well.

Error bars for  $[H^+]$  were based on the rated variability of the pH probe used, converted into  $[H^+]$  units. Error bars on the OC concentrations were based on the variability in the replicate semi-continuous OC measurements conducted during each sampling period (typically,  $n > 20$ ). Error bars on yield values (requested below) incorporate variability in replicated hydrocarbon measurements and OC measurements during each sampling period. Error bars on absolute humidity were based on variability in the measured temperature and RH data, converted to absolute humidity on a 5-minute basis throughout each sampling period ( $n > 200$ ). Text has been added following the presentation of Figure 1 (Line 253), Figure 3 (Line 363), and Figure 4 (Line 387) clarifying the basis for the error bars presented.

L214 – What is the [SO<sub>2</sub>] background?

As given in Table 1, a background SO<sub>2</sub> concentration of 11 ppb was detected in the absence of SO<sub>2</sub> addition to the chamber. This reading was likely due to a small hydrocarbon interference on the SO<sub>2</sub> monitor, as this stage of the experiment was conducted last and the monitor's scrubbers had been subjected to significant hydrocarbon, SO<sub>2</sub>, and aerosol concentrations in prior stages.

L579 – I believe figure 4 should have error bars similar to those in Figures 1,2,3 and 5.

Figure 4 has been revised to include error bars on both axes.

General – additional details that would provide useful insight include how SO<sub>2</sub> and particle sulfate were measured; the temperatures at which experiments were conducted; and whether any oxidant source was added (and how much) to initiate the oxidation of the hydrocarbons.

Additional clarification has been added to the methods section to identify the SO<sub>2</sub> monitor employed (Line 147):

“NO and NO<sub>y</sub> were measured with a TECO model 42C (Franklin, MA) oxides of nitrogen chemiluminescent analyzer, SO<sub>2</sub> was monitored by pulsed fluorescence detection (TECO, Model 43A), and O<sub>3</sub> was measured with a chemiluminescent ozone monitor (Bendix Model 8002, Lewisburg, WV).”

and the measurement of particle sulfate (Line 157):

“Extracts were analyzed for sulfate (SO<sub>4</sub><sup>2-</sup>) ions using a Dionex DX500 Ion Chromatography system equipped with an electrical conductivity detector. Anion analysis was conducted using a Dionex IonPac AS14A column and an isocratic 4 mM sodium carbonate/0.5 mM sodium bicarbonate eluent.”

Clarification of experiment temperatures for the isoprene/SO<sub>2</sub> experiment and the 1,3-butadiene vs. [H<sup>+</sup>] experiment have been added to the text, while Table 4 has been updated to include temperature ranges for the RH experiments, as requested above by Reviewer #1. Only NO was used as an oxidant in the experiments.

Technical corrections: The manuscript is largely free of typographical and grammatical errors.

L90 – an extra space in “by anthropogenic”

Corrected

L109 – “of” should be “in”

Corrected