We thank the reviewers for careful reading and helpful comments that improve the quality of the manuscript. Reviewer comments have been copied followed by our responses in bold.

R1 (Anonymous Referee #2)

General Comments
This paper presents evidence of formation of organonitrates, organosulfates, and mixed nitrate-sulfate organic compounds from glyoxal. Their formation is attributed to aqueous phase processing of glyoxal and its hydrated forms. While photochemistry of gas-phase species enhanced the formation of the organitrogen and organosulfar compounds, the authors present reasonable evidence that this was due to enhanced formation of HNO3, which partitioned into aerosol and enhanced aqueous processing.
Also, the products were formed during photochemical experiments were also formed without UV irradiation. An existing model of aqueous-aerosol glyoxal chemistry was modified to include some new reactions and partitioning of glyoxal. The formation of these interesting organitrogen and organosulfur compounds seems clear, supported by identification with mass spectrometry and a fairly straightforward experimental design.
The data to support conclusions regarding kinetics of these reactions and subsequent modeling is limited, and it is not clear if any strong conclusions can be made by comparison with a kinetics model. The main result of this work is the identification of the products, with the potential of their formation in atmospheric aerosol via the aqueous chemistry presented here.

R1C1) No attempt was made to track the total amount of oxidized forms of nitrogen (e.g. NOx, organonitrates, HNO3), and this should be done during revision. For example, can the observed changes in gas-phase NOx levels be reasonably attributed to known sinks?

Response) We did not attempt to measure HNO_3 uptake quantitatively. A FACSIMILE model predicts ~500 μM of HNO_3 uptake in the aqueous phase after 3 hour irradiation when initial conditions are 10 ppb of NO, 0 ppb of NO_2, 10 ppb of O_3 and 500 ppb of an organic compound in the gas phase (glyoxylic acid). This concentration of HNO_3 is comparable to that of inorganic constituents in wet aerosols (200 μM of ammonium sulfate/sulfuric acid). We added this point at the end of section 3.3.

"We also estimate the concentration of HNO_3 taken up into wet aerosols by including chemistry of NO_x, HO_x, peroxy radical, HNO_3 partitioning into a FACSIMILE model. ~ 500 μM of HNO_3 uptake in the aqueous phase is predicted after 3 hours of irradiation when initial conditions are 10 ppb of NO, 0 ppb of NO_2, 10 ppb of O_3 and 500 ppb of an organic compound in the gas phase (glyoxylic acid). This concentration of HNO_3 is sufficient to form organonitrates with glyoxal and comparable to that of other inorganic constituents in wet aerosols (200 μM of ammonium sulfate/sulfuric acid)."

R1C2) The lack of detection of glyoxal or its hydrated forms in humidified ammonium sulfate aerosol, even at the beginning of the experiment, is somewhat puzzling and must be explained further.

Response) Thank you for pointing this out. We reinvestigated and found that m/z^+ 131 ([glyoxal + $2H_2O$ + Na]$^+$) was actually detected in 15 and 30 minute samples. But m/z^+ 131 that we detected in 0 minute sample was an imine (C4H7N2O3), which appeared to overlap the glyoxal peak. So, a decay plot cannot be constructed.

We changed the sentence in the paragraph (line 15, page 8) as follows:
"(glyoxal was also detected for AS aerosols in the humid chamber; however, since it was only detected in 15 and 30 minute samples, no decay plot was constructed)"

We also added the following in the text (line 12, page 8):

“131 (= [M + H_2O + MeOH + Na]$^+$)”

This work is significant in the identification of formation of organitrogen and organosulfur compounds from glyoxal chemsitry. Therefore I recommend this work for publication, pending revisions. Fundamental points still need to be addressed, and a number of clarifications are required prior to publication, as detailed below.

Specific Comments
R1C3) (2, 39) It should be noted that the low volatility of glyoxal results largely from the high level of hydration that occurs upon dissolution in water.

Response) Clearly glyoxal undergoes hydration, but immediately hydrated glyoxal forms oligomers via acid catalysis and organic-inorganic complexes in the presence of inorganic constituents. These are likely to be SOA from glyoxal. And these points were already addressed in the previous paragraph (line 10-18, page 2).

We have modified that sentence to clarify the reviewer’s point:
“Water soluble organic compounds like glyoxal and methylglyoxal hydrate and form oligomers through hemiacetal formation and aldol condensation, especially in evaporating droplets.”

R1C4) (4, 6) It is has been shown that drying can induce chemistry in aqueous aerosols. (1-3) The aerosol in this study contained glyoxal prior to drying and addition to the chamber. Were there any indications that chemistry occurred during that drying process?

Response) Yes. In Fig. S6, solutions and aerosols in the chamber at 0 minute were directly compared. Imines and acid-catalyzed oligomers were found in the aerosols. This is discussed in the text (line 13, page 10).

R1C5) (4, 15) The humidifying process should be described in further detail. It is currently described as the chamber being filled with clean dry air and then humidified. It doesn’t seem feasible that 90% RH can be reached with the chamber initially full of dry air.

Response) This humidifier was developed by modifying an existing commercial humidifier. Water spray and evaporation pan were specially designed to generate water steam rapidly. While adding water vapors into the smog chamber, we monitored SMPS to ensure that no water droplet was introduced. This device will be requested for patent in the future, so we cannot discuss more in details.

We added:
“This humidifier was developed by modifying an existing commercial humidifier. Water spray and evaporation pan were specially designed to generate water steam rapidly. While adding water vapors into the chamber, we monitored SMPS to ensure no water droplet was introduced.”

R1C6) (4, 12) Please elaborate on the relevance of your gas and particle phase concentrations to the atmosphere. Although the goal of this study is largely to show the potential source of these compounds and the link to aqueous processing, the relation to the atmospheric conditions should be addressed further.

Response) We added the following:
“Concentrations of NO_x, O_3, and particle mass in smog chamber can be related to a moderate haze condition in urban areas, particularly observed in Seoul or Beijing.”

R1C7) (4, 23) The use of E-AIM will also provide, as you note, the pH of the aerosol, yet pH is not reported here. pH will affect particle equilibria, partitioning, and may change the resulting chemistry. It is certainly an important environmental variable that should be reported for all experiments in Table S1. A general comment on pH and potential effects should be included in your updated discussion, particularly since acidity was a major aspect of your experiments (sulfuric acid seed vs. ammonium sulfate seed).

Response) We have added pH values in Table S1. It appears acidity affects oligomerization in SA aerosols, and this is discussed in line 22-29 on page 10.

R1C8) (5, 13-19) This section has the heading ": : : and 226", but no mention is made of m/z 226.

Response) We change the section title to:
"MS/MS analysis for m/z^- 147 and standard MS analysis for m/z^- 147 and 226"

R1C9) (6, 12-15) The authors observed that experiments that are similar, except for the presence of glyoxal (#2 and #7), had very different NOx chemistry, but do not explain this. The sinks and consequences of gas-phase NOx should be more clearly discussed, particularly in light of your observations. For example, if NOx is converted to HNO3 and partitions to aerosol, pH could be significantly altered.

Response) Please see our response for R1C1 regarding sinks of NOx to HNO3. NO2 is effectively formed by peroxy radical-NO reactions (#2), but is only slightly increased due to the lack of peroxy radicals when there is no glyoxal in the beginning (#7). This point is already discussed in line 10 on page 6. There was no evidence of enhanced oligomer formation by HNO3 uptake while more oligomers were observed in SA aerosols. We modified the text (line 3, page 10):

"However, acidity effects on oligomer formation requires further study because sulfuric acid in SA aerosols appears to enhance oligomerization while photochemically formed nitric acid does not."

R1C10) (7, 9-11) Were NO2+ to be formed in any significant amount, would this now be a potentially important reactive species (nucleophile) in your aerosol? Are there any indications that this is the case?

Response) We did not attempt to measure NO_2^+, so heterogeneous reactions of NO_2^+ is beyond the scope. In this paper, we focus on nitrates and organonitrates. We just mention this since no HNO_3 was observed in SA aerosols.

We have now added:
"If NO_2^+ were formed in a significant amount, it could be an important reactive species. However, measurement of NO_2^+ and investigation of its potential role is beyond the scope of this study."

R1C11) (8, 15) The authors state that no glyoxal peak was observed in mass spectra for the humid chamber AS aerosols, yet you do observe organonitrate products (Fig. 1). Does your model suggest complete and rapid conversion of glyoxal to products? Given the importance of ALW for partitioning of glyoxal, it is puzzling that AS aerosol under humid conditions does not contain glyoxal. This important point was dismissed by the authors.

Response) See our response for R1C2.

R1C12) (9, 32) The aerosols evaporate to maintain equilibrium at the RH conditions of the chamber, not due to surface area considerations. What comment about surface area was intended?

Response) This has been changed in the text to:
"When the solutions are atomized and introduced into the smog chamber, water evaporates to equilibrate to the chamber RH, and concentration of solutes increase."

Technical Comments
R1C13) (Page 1, Line 13) change to read "or sulfuric acid particles"

Response) It was already written as "or sulfuric acid particles."

(Page 1, Line 33) This sentence is awkward, but it makes an important point that SOA(aq) is likely to improve model predictions. Please make this sentence clearer, perhaps split into two.

Response) Now it reads:

"Including SOAaq is likely to improve model predictions, which currently underestimate the ambient concentration and oxidation state of organic aerosols. Water soluble organic compounds with a small carbon number (C2-C3) are not considered precursors to SOA formation through gas-phase chemistry and vapor pressure driven partitioning (Pankow, 1994) because of their high vapor pressure. However, they are potential SOAaq precursors."

R1C14) (2, 12) Add references 4 and 5.

Response) We add suggested references.

R1C15) (2,18) Add reference 6.

Response) We add suggested references.

R1C16) (2, 20) change to read "..compounds, OH radicals, and water.."

Response) Now it reads as the reviewer suggests.

R1C17) (3, 6) The importance of more realistic aerosol composition should be noted here.
Ambient aerosol will have a wide range of organic compounds in addition to those derived from glyoxal.(Refs 7,8) Recent work suggests that compounds like glyoxal will from condensation products (acetals, etc.) with these other aerosol constituents.(Ref 9)
This could affect the chemistry studied in this work, by reducing the amount of glyoxal available for reaction and potentially changing the product distribution. The authors should address the effect of actual ambient aerosol composition.

Response) Glyoxal is a surrogate of water soluble organic compounds in ambient wet aerosols. Radical and non-radical reactions of water soluble organic compounds in wet aerosols are expected to be seen in our glyoxal reactions. Glyoxal undergoes self-oligomerization through hemiacetal formation and aldol condensation leading to light absorbing products (Shapiro et al., 2009). Ammoniums, sulfates and nitrates are main inorganic constituents (Zhang et al., 2007), and glyoxal reacts with them. OH reactions of glyoxal produce dicarboxylic acids (e.g., oxalic acid), which are also expected to be the products of water soluble organic compounds.
These non-radical reactions compete with OH reactions. In our smog chamber experiments, non-radical reactions are more dominant than OH reactions in the condensed phase and we expect this is true for water soluble organic compounds in ambient wet aerosols.

We added the following in the sentence:
"glyoxal is used, as a surrogate of water soluble organic compounds in ambient wet aerosols, to explore non-radical and radical reactions in the condensed phase leading to SOA."

R1C18) (3, 23) remove the first word : "the"

Response) Now "the" is removed.

R1C19) (3, 35) change to read ".., liquid water, and : : :"

Response) We do not understand this request. Perhaps the page or line number the reviewer is referring to is incorrectly written??

R1C20) (5, 30-31) change to read ": : :08C11) and not likely nitric acid adducts.."

Response) Now "and" is inserted

R1C21) (5, 37) change to read "..Cole, 2000), and MIDAS does not propose.."

Response) Now "while" is changed to "and."

R1C22) (6, 12-13) change to read "Experiment #2) also shows significant.."

Response) Now "the" is removed, as suggested.

R1C23) (6, 16) This is an interesting style of using an introductory question. It would be better to use a direct statement rather than giving the reader some suspense. Ambiguity impedes clarity. Please rephrase as a direct statement, such as "Aqueous phase chemistry and photochemistry may lead to volatile products that contribute to gas phase peroxy radicals"

Response) Now it reads as the review suggests:
"Photochemistry on wet aerosols may lead to volatile organic products that contribute to gas-phase peroxy radicals."

R1C24) (6, 37) and (7, 1) and throughout the manuscript, change to read ": : :after 3 hours of irradiation: : :"

Response) Now we changed according to the reviewer's suggestion.

R1C25) (7, 3-5) While heterogeneous reactions are a possible source, do the authors consider OH + NO2 a source of HNO3? Is this included in the model?

Response) We include this as an aqueous phase reaction. NO_2 concentration in the aqueous phase is determined by the Henry's law constant. The contribution of this reaction to HNO_3 is, however, small.

R1C26) (7, 12) change to read "Figure 2 suggests: : :"

Response) We removed "also" to read as suggested.

R1C27) (8, 3-4) change to read "During irradiation, oxalic acid was formed in the humid chamber, shown by UPLC-Q-TOF-MS detection of m/z- 89: : :”

Response) We changed according to the reviewer’s suggestion.

R1C28) (9,28) through (10, 29) The time-resolved data should be addressed within the context of other studies. Particularly for the reduced nitrogen species (imines, imidizoles, etc.) Studies have looked at this reaction under a wide range of conditions, which should allow comparison.(Refs 10-12)

Response) We already discussed previous studies of nitrogen-containing organics (line 13-15, page 2). So we have added the suggested references (10-12) there.

R1C29) (10, 18) change to read “: : : because aqueous phase reactions of glyoxal with ammonium form imines...”

Response) Now we remove “in the” to read as suggested.

R1C30) (10, 22-23) change to read “: : :form oligomers and imines. In SA aerosols the formation: : :”

Response) We split the sentence into two as the reviewer suggests.

R1C31) (11, 8) change to read “: : : during the daytime. Notably, nitrate concentrations: : :” Figures

Response) Now we removed “And,” as suggested

R1C32) Scheme S1. This should be placed into the main manuscript. You discuss extensively the formation of these organonitrates, so this should not be supplemental.

Response) We agree. Now Scheme S1 is Scheme 4. The previous Scheme 4 is now Scheme 5.

R1C33) Figure 1. This figure should be a 4 panel grid, with the spectra for humid conditions on the top row, and dry conditions on the bottom row, with AS results on the left and SA results on the right. It is difficult to compare in a single column. Each figure (a-d) should have a label denoting the aerosol type and the humidity level.

Response) Figure 1 is now a 4 panel grid as the reviewer suggests.

R1C34) Figure 3. The legends must be moved to the top right corner to avoid confusion between the data and the legend. R-squared should be reported to at most 3 decimal places (0.001). The linear fits do not need to fully displayed, only the time constants. The linear fit intercepts should all be 1.0. Instead of presenting the equations, you should label the plots with the effective lifetime or the half-life of the glyoxal.

Response) Legends are now placed on the top right corner. Instead of the equations, the rate constants, k (min-1), are used. R-squared has now 3 decimal places. Y-intercept value (at t = 0) for A is now 1.

R1C35) Figure 4. The same 4-panel grid format as suggested for Figure 1 should be used.

Response) Figure 4 is now a 4 panel grid as the reviewer suggests.