Response to Referee Comments:

The authors would like to thank all the reviewers for their thoughtful and helpful comments. Below are our point by point responses to each of the reviewer's comments where our responses are in bold print. As a result of the reviewers comments the manuscript has been significantly improved and we believe it should be publishable in ACP.

Reviewer #1

General Comments:

The authors present results from studies where ambient urban air was exposed to either acidic or non-acidic sulfate seed aerosols. Under neutral conditions, the authors show that primary oxygenated species condensed on the seed aerosol, increasing the aerosol organic mass. In the presence of acidic seed, the uptake of primary oxygenated organics was enhanced relative to the neutral seed experiments which was attributed to non-reversible oligomerization reactions. Particle acidity correlated with the rate of increase of higher MW products, further indicating these oligomerization reactions are acid catalyzed. Although the impact of this organic aerosol source is small when considering typical SOA loadings in regions where this chemistry could be expected (urban, downwind regions), it could be on the same order of magnitude as POA. As processes and compounds contributing to organic aerosol formation and growth are not fully understood, this manuscript provides valuable insight into a previously unknown source of oxygenated organic aerosol in the atmosphere which will be of interest to the ACP readership.

The manuscript is well written, however there are some data and conclusions that need clarification, as detailed below. In particular, the presented data and conclusions are based on whether the experiment was with either neutral or acidic seed aerosols; however, the grouping of experiments based on this criterion is inconsistent in the manuscript. Also, in most cases, only data from select experiments within each seed group are included in the figures. This makes it difficult to determine if it is valid to draw clear conclusions based on the type of seed aerosol. I recommend this manuscript for publication after addressing this and the following comments.

We thank the referee for the important points raised above. We have addressed these issues as they arise in the more specific comments provided by the referee below.

Specific Comments:

P 29071, lines 2-3: “Typically, SOA dominates the OM mass. . .” This should read either “. . .OA mass...” or remove “mass” and define OM.

We have corrected this line to read: "*…OA mass…*"

P 29071, lines 6-7: What do the authors mean by, ". . .and oligomer formation via aerosol-phase chemistry potentially increasing in importance."? Is our knowledge of these reactions increasing or are they truly contributing more to aerosol phase chemistry with time?

We meant to state that the knowledge of these reactions is increasing which if included in models may reduce the model measurement discrepancies. The line now reads:

"Oligomer formation via aerosol-phase chemistry is of potential importance to overall SOA formation (Nguyen et al., 2011; Hall & Johnston, 2011), as is the formation of semi-solid particles which affects gas-particle partitioning (Vaden et al., 2011; Perraud et al.2012). Neither of these two processes are adequately parameterized in models but may help to explain discrepancies between models and observations."

P 29071, lines 6-7: With regards to the statement, ". . .traditional oxidation mechanisms. . . unable to account for SOA observations.", currently unknown oxidation mechanisms are not the only possible source of the discrepancies between models and measurements for SOA. For example, another source may be the treatment of particles as liquids with regards to partitioning in current models. Recent studies (e.g., Cappa et al.; Kuwata et al.; Perraud et al.; Vaden et al.; Virtanen et al.) have shown that particles can be non-liquid, which can affect partitioning and reactivity and thus model calculations.

We thank the reviewer for this important point. We have added text to note this additional source of potential discrepancy. The relevant lines now read:

"*….as is the formation of semi-solid particles which affects gas-particle partitioning (Vaden et al., 2011; Perraud et al.2012)). Neither of these two processes are adequately parameterized in models but may help to explain discrepancies between models and observations*".

P 29072, line 18: It is unclear what is being contrasted in this paragraph. The second half of the paragraph applies to acidic seed aerosols, but it is not clear if the first half of the paragraph is meant to refer to the neutral seed or to both neutral and acidic seeds. Please clarify or remove "In contrast."

We have clarified this sentence. It now reads:

"The results demonstrate that the condensation of existing ambient primary species will lead to significant oxygenated OA on neutral particles, prior to gas-phase oxidation. The uptake of ambient gaseous organics to acidic aerosol and subsequent aerosol-phase chemistry will also result in high MW species and/or oligomers which significantly enhance aerosol oxygenation."

P 29073, line 17: Was the elemental analysis carried out using APES? If so, add references for Aiken et al.

APES is part of PIKA which was used for analysis. We have now added both Aiken references.

P 29074, lines 11-12: Please clarify that exposure of H2SO4 aerosols to organic free air and NH3 resulted in "no measurable organic uptake."

We have clarified this sentence which now reads as:

"Exposure of generated H_2SO_4 particles to organic free air and excess gaseous NH_3 resulted in immediate aerosol neutralization and no measurable organic uptake (0.03±0.03 ug m^{-3})."

P 29075, lines 3-5: I disagree that ". . .those experiments with excess NH3 fall closest to the best fit line." I don't see a clear trend in [NH3/SO4]i and agreement with the best fit line. If there is a trend, what does this imply or what is the explanation for this? Either remove this part of the sentence or discuss and show this more clearly.

It was not our intent to show that within the range of initial NH3/SO4 of the figure that there is a relationship. We only meant that all the experiments with excess NH_3 (regardless by how much) which are neutral (or close to being neutral) are approximately along the line, in contrast to the highly acidic ones (red points). We have therefore removed the color scale, to avoid confusion and removed the line in question. The lines now read:

"According to Figure 2A, the mass of organics taken up is proportional to the mass of the sulphate seed, particularly for those experiments with neutral particles, and those which are only slightly acidic (1.5< $[NH_4/SO_4]_f$ <2)."

P 29075, line 16: ". . .the average organic spectrum for the experiments with highest [NH3/SO4]i in the present study are shown in Fig 2b." Please state in the text which specific experiments are included in this average. It is listed in the figure legend only. What is the rationale behind only averaging the experiments with the highest [NH3/SO4]i, as opposed to averaging all experiments categorized as neutral (E4-E14)? If there is a dependence of the mass spectra on [NH3/SO4]i which is considered neutralized, this should be discussed in the text.

We have now included in the text, a description of the spectra used. This now reads as:

"The AMS organic mass spectrum from Li et al. (2011) and an average organic spectrum for the first 2 minutes in the present study are shown in Figure 2B. To be consistent with the neutral seed particles utilized in Li et al., 2011, only experiments considered fully neutral (E5 - E7, E9 – E13) in the present study are used in computing the average spectra. However, even

slightly acidic spectra (E4, E8, and E14) have initial organic spectra similar to that of Figure 2B."

There are small differences in spectra in all the experiments due to many factors, but most importantly the concentrations and mixture of ambient gases present. Also, since a range of ammonia concentration was present, some experiments were within the uncertainty in the neutralization ratio, or neutralized slightly slower than expected as reported in Liggio et al., 2011. The Li et al paper (2011) generated particles via atomization which were always completely neutral, thus to be most representative of a neutral particle in these experiments (to compare with Li et al) we had chosen to use the experiments with the highest NH3/SO4 (initial). This avoids the potential for reactive uptake which could occur for a very short time prior to or during neutralization. We have regrouped the experiments as described below. Using the average spectra of all neutral experiments from the new grouping does not result in a spectra significantly different than Li et al 2011 (r2=0.9). We have now used the average of E5 - E7; E9-13 in this and subsequent figures.

P 29078, lines 23-24: The authors have provided approximate O:C values/ranges for the gasoline derived POA and OA from this study and Li et al (2011). Can the authors also provide literature values/ranges of O:C for HOA and SOA?

We have now added the literature values and reference.

P 29080, line 4: The statement ". . .orders of magnitude above the noise level. . ." seems to be an exaggeration, even taking into account the log scale. From the peaks which are on scale in Figure 5, most peaks seem to be roughly an order of magnitude or less. I suggest changing "orders of magnitude" to "an order of magnitude".

We have made the suggested change.

P 29081, line 14: It is unclear if the O:C ratio is associated with m/z >300 or for the entire mass range. Based on the following discussion in the text, I am assuming it is for the entire range, however the use of the word "associated" makes this unclear.

We have clarified the text which now reads as:

"The fraction of the total organic fragments attributed to high MW fragments (using (m/z>300/Total Org) as a surrogate) and the organic O:C ratios for three experiments with an additional NH_3 pulse is given in Figure 6A. The O:C ratio is determined for fragments up to 150 amu, which encompasses >95% of the total organic mass."

Section 3.2.2: In Figure 6a, the O:C ratio during E14, which was grouped with the neutral seed experiments (P29074 lines 15-20) and not with the acidic seed experiments at the beginning of this section (P 29079, lines 15-16), is in fact increasing from _0.15 at the start of the experiment to _0.33 after _250 minutes. However, the authors state, ". . .increases in the O:C ratios over time were not observed for experiments with neutral aerosols. . ."

We agree that the overall grouping of experiments can be improved. We have now re-grouped the experiments to include experiments based upon their final NH4/SO4 into those that are very acidic, those that are slightly acidic (within uncertainty~25%) or that are not neutralized instantly, and those that are neutral immediately (ie: within 25% of 2.0). We have also added text to better explain the groupings which reads:

***"These ambient exposure experiments can be separated into three groups based upon their final [NH_4/SO_4] (Table 2); those which begin with sufficient NH_3(g) in the chamber initially to immediately and fully neutralize the aerosols as indicated by the final molar neutralization ratio ([NH_4/SO_4]$_f$≈2, E5 – E7, E9 – E13); those in which the aerosols remained highly acidic ([NH_4/SO_4]$_f$<1; E1 – E3); and those experiments which are slightly acidic (1.5<[NH_4/SO_4]$_f$ <2; E4, E8, E14) based upon an approximately 25% uncertainty in determining [NH_4/SO_4]$_f$. "*.**

Experiments which were instantly neutral indeed did not have an increasing O:C. E14 clearly does not fall into this group as it is slightly acidic.

(P 29082, lines 1-2) Do the authors mean that the rate of increase in the O:C ratio does not change with the NH3 pulse?

We meant to state that the O:C ratio does not evolve in time (ie: constant) for neutral experiments, based upon the new groups defined above, and regardless of additional NH3 pulse. We have clarified this point in the text which now reads:

"Changes in the O:C ratios over time were not observed for experiments with completely neutral aerosols (E5-E7; E9 – E13), suggesting that acidity played a key role in the evolution of the O:C ratios observed in the acidic aerosol experiments."

Also, the m/z>300/Tot Org is increasing with time for E14 prior to the NH3 pulse, although for the neutral experiments, it was stated that the mass remained constant after the initial uptake in the first 2 minutes.

Based upon the new groupings above, E14 is not considered fully neutral. However, changes in mz300/total Org only means that the relative proportion of larger species is changing, not that the total organics is changing. (ie: the mass remains constant)

Perhaps it would be informative to include the m/z>300/SO4 data in Figure 1a on the right-hand axis as done in Figure 1b, if in fact the fraction of m/z>300 is increasing while the total organic loading is maintained in the neutral seed experiments.

We did not intend suggest that the fraction of large m/z is increasing in neutral experiments. This is only observed for acidic experiments, and particularly the

most acidic ones. Including m/z>300/SO4 for fully neutral experiments in fig 1a is not possible as these large fragments are not consistently observed in those experiments and/or at the noise level. We have clarified the text in this regard which now reads:

"….as large as ~600 amu are approximately an order of magnitude above the noise level (note Log scale). Conversely, significant high MW fragments were not observed for the fully neutral particle experiments."

The large increase in m/z>300/Tot Org following the NH3 pulse in E14 is not accompanied with the same large increase in O:C observed for the acidic E3, instead the O:C continues the steady increase observed before the NH3 pulse. Can the authors comment on these points?

We agree that it is not nearly as evident as it is for E3, likely because the acidity level in E14 was significantly less. We have now decided to show another acidic experiment in addition to E14, to be consistent and to demonstrate this effect is indeed occurring and is more prominent under acidic conditions. Additional text clarifying the figure has been included:

"*Figure 6A demonstrates that the relative importance of high MW products increases as a result of aerosol neutralization (shaded regions) at the expense of reversible products, and that this effect is more prominent for the most highly acidic experiments."*

In the caption for Figure 6b, I see that E14 (and E4 and E5) are now designated as experiments which remain acidic. Is this because the final NH4/SO4 is less than 2? Following this criteria, E6-9 and E11 should also be regrouped and included in Figure 6b. The regrouping of E4, 5 and 14 is not mentioned in the text and is confusing as they were originally grouped with the neutral seed experiments.

We agree that the grouping needs to better categorize the seed aerosol acidity, and have changed and clarified the grouping as described above. Based upon the new grouping fig 6b includes the most acidic experiments only (E1-E4; E14). The amount of mass taken up in some of the only slightly acidic experiments (E8) is very similar to that of fully neutral experiments, and thus have elemental compositions (O:C, H:C) that are difficult to ascertain due to the low amount of mass, or not changing as noted previously. We believe that the evolution in VanKrevelan space is a phenomenon which occurs under more highly acidic conditions. Figure 6B has been modified to reflect this, and text has been added to clarify this point:

"*For the most highly acidic cases, where sufficient organic mass was taken up on the seed aerosols to allow for a reliable elemental composition determination (E1 – E4; E14), the data fall along a slope of approximately -1.5."* **and**

"…the slope in this study is facilitated by the aerosol-phase chemistry, enhanced by particle acidity. As noted above, such an evolution in elemental composition is only observed for the most acidic experiments, highlighting the importance of acidity in the reactive uptake and hence evolution of organic aerosol O:C."

Are the changes with NH3 pulse observed for all experiments where it was added? For the acidic conditions, an NH3 pulse was only added for one acidic experiment. However, an NH3 pulse was added for E4, E5 and E14. Was the behavior shown in Figure 6a for E14 also observed for E4 and E5? A sentence added to the text would clarify this.

An ammonia pulse was only added in one neutral experiment (E5) and this behavior was not observed. This behavior was observed somewhat in the other experiments, but was most pronounced for the most acidic experiments. We have clarified the text which now reads:

"This behaviour was most prominently observed in experiments with the highest acidity, while addition of excess ammonia during a neutral aerosol experiment (E5) did not result in any significant loss of organics"

Also see our response above.

Table 1: It is useful to have the individual mixing ratios for toluene, benzene, terpenes and isoprene. However, to facilitate comparison of the experiments, it would be nice to also have the final values. Can these be added to the table, perhaps in parentheses following the individual values?

Given that wall loses in the chamber for these gaseous species is minimal, the values in Table 1 are the final values.

Figure 1a: Why were these 3 neutral seed experiments included and not all the neutral seed experiment time traces?

We attempted to show those experiments which had the highest initial ammonia/SO4 ratio. However, given the re-grouping above we have now included more traces, while attempting to keep the figure uncluttered. We have also added text to the beginning of section 3.1:

"This increase in Org/SO_4 occurred faster than the AMS measurement time resolution (2 min) for non-acidic aerosols in particular (but also slightly acidic aerosols) after which the Org/SO_4 remains approximately constant (Fig 1B). "

Figure 1b: Number 1 near arrow for addition of NH3 is not mentioned in the text or caption.

The arrow is indeed mentioned in the caption, but now also in the text (section 3.2.1).

Figure 2b: The authors state that the best fit line is through shaded points only, however all the data points are colored. There is also the shaded region. Please clarify in the caption, perhaps stating fit only includes the data denoted with square markers.

We have removed the shading as it is not discussed in the text, and clarified as suggested in the caption.

Figure 2b, 3 and 4: What does the subscript “a” on the y-axis label denote?

The “a” denotes that the signal has been normalized to the total organic signal. We have added this in the captions for these figures.

Figure 3: Please add A, B, C and D labels to the individual graphs (not just legend subscript), as done in Figures 1 and 2 for example.

We have made the suggested changes.

Figure 6a: Why is the O:C data for E3 not shown for the entire experiment? It stops at 180 min, whereas the corresponding m/z>300/SO4 trace for this experiment continues to _300min. There is a sharp increase after the addition of the NH3 pulse and I would like to know if this value continues to increase or the plateaus.

The O:C determination is quite poor after this point, and very noisy. This was likely due to a low overall signal after this point. The quantification of mass is more sensitive than the O:C determination, as it depends upon the quality of fits for individual fragments, which are weaker near the end of experiments. Also, the time axis is somewhat confusing here, since it was shifted to put the time after NH3 addition on the same scale. We have properly scaled this in the new figure, which now shows that the region in question is beyond 300 min where the signal was low due to particle wall loses.

Technical Comments:

P 29071, line 3: “remains” -> “remain”

We have made the suggested change

P 29074, line 25: Awkward wording of “which for non-acidic aerosols is essentially complete.”

We have clarified this line which now reads:

“This increase in Org/SO_4 occurred faster than the AMS measurement time resolution (2 min) for non-acidic aerosols in particular (but also slightly acidic aerosols) after which the Org/SO_4 remains approximately constant (Fig 1B).”

P 29075, line 10: Should read, “. . .and the fast organic uptake was found to be. .

We have made the suggested change

P 29078, line 17: “is” -> “are”

We have made the suggested change

P 29079, line 20: Lower case “Aerosol-phase”

We have made the suggested change

P 29086, lines 24-25: In the Jimenez, et al. reference, there is a web address inserted in the author list.

Corrected.

All Figures, but particularly 2, 3 and 6: It is very hard to see the figure labels, legends, etc. when printed at 100%. Please make labels larger for better readability.

We have made the suggested change

Figure 2a: Dashed line in the legend is removed from the description (Li et al., 2011)

Corrected.

Figure 2b: The “41” label is partially missing.

Corrected.

Figure 5: X-axis “m/z” label on the main graph is partially missing.

Corrected.

Table 1: Footnote e: Capitalized “limit” or lowercase “ below detection” in “Below Detection limit”.

Corrected.

Table 1: Final column heading (Additional [NH3] Pulse) is missing units.

We have added the units.

Table 2: Subscript on E14 (NH4/SO4)f entry should be “d”, not “g”.

Corrected.

Reviewer #2

General Comments:

In this manuscript, the authors perform chamber experiments examining the uptake of oxygenated organics from filtered ambient urban air onto neutral and acidic sulfate seed particles. The authors measure fast, but relatively small uptake of oxygenated gases onto neutralized seed aerosol that scaled with seed mass. In the presence of acidic sulfate aerosol, the authors measure continuous uptake of more substantial amounts of organic. Simultaneously, they observe changes in the OA mass spectra and O:C consistent with formation of high-MW oligomers. The manuscript is relatively clearly written and the subject will be of interest to readers of ACP. A chemical mechanism explaining the uptake on the acidic particles is presented and is supported by the data. These observations are also broadly consistent with literature studies showing organic oligomerization reactions in acidic aerosol and with current understanding of organic aerosol (OA) formation.

The more surprising results come from the observations of uptake of organics onto neutral seed aerosol, which make up the bulk of the experiments presented in the manuscript. For these experiments, the authors do not present a mechanism that can explain their observations, which are difficult to interpret in the context of the current understanding of OA formation. Given the lack of an explanation for their neutral seed observations, it is difficult to rule out that the data are an experimental artifact.
The authors should offer some plausible mechanistic explanation for dilute organic gases condensing or reacting on the neutral seed aerosol. The explanation the authors currently offer is reported to be of minor importance just a few pages earlier in the manuscript. Providing additional experimental detail, such as the phase of the neutral seed particles, the total aerosol loading involved, and the additional details on the gas-phase hydrocarbons, would potentially clarify possible mechanisms and convince readers and reviewer(s) that their observations are applicable to the atmosphere. After these revisions, the manuscript should be publishable in ACP.

We thank the referee for the important points raised above. We agree that under neutral seed conditions the mechanism of uptake was not well presented, and more difficult to put into an atmospheric context. We have addressed these issues as they arise in the more specific comments provided by the referee below.

Major Specific Comments:

As the manuscript is currently written, it is difficult to assess whether the OA formation/ condensation observed on the **neutral seed** experiments is a robust phenomenon one could expect to occur in the ambient atmosphere or a result of an experimental artifact. I'm having a hard time interpreting their observations in the context of what is current known about OA formation. .

We agree that the organic incorporation to neutral seed is difficult to reconcile with traditional OA formation mechanisms as it is written in this manuscript, and the lack of a clear mechanism in this case also makes interpretation difficult. However, we do not believe this is a result of experimental artifact or uncertainty as the uptake on neutral seed was reproducible, well above the noise level of the instruments, and entirely consistent with the observations of Li et al 2011 using a different experimental approach. Our current hypothesis is that much of this uptake is simply due to solubility of polar gases, as was demonstrated in the experiments of Li et al., 2011. Although we did not explicitly state this, it is implied. However, we have clarified this mechanism and the discussion throughout the manuscript as discussed in our response to the specific points (1-5) below.

Currently, the authors suggest that hydration of olefins under acidic conditions may explain the uptake (P29079, lines 6-11). However, on P29077, lines 17-23 the authors argue that the importance of reactive uptake on acidic seed is minor.

We agree that the two statements made on pg 29079 and 29077 may seem somewhat inconsistent with each other as written. On pg 29077 we are attempting to state that reactive uptake similar to that during the acidic experiments is likely of a minor importance on NEUTRAL seed particles. On pg 29079 we are essentially repeating what was said on pg 29077 in that hydration reactions (one of many possible reactions), is likely minor for both acidic and neutral particles. We have clarified the text on 29079 such that they are consistent by deleting lines 11-13 and adding the following text:

"Given that reactive organic mass uptake enhanced by acidity is of minor importance for neutral experiments (noted above), it is unlikely that any aerosol reactions such as olefin hydration (Liggio et al., 2008, Liu et al., 2010) would explain the added oxygen within the neutral seed aerosols."

This does not change any conclusions.

The authors also argue that incorporation of organic during nucleation of the sulfate seed is unimportant and that repartitioning of organics from the filtered aerosol to the seed aerosol is unimportant. Finally, the authors report that there was little or no oxidant present in the system.

We continue to believe that these points apply in this case based on the arguments in the manuscript (pg 29077-78).

In the absence of reactive uptake or incorporation of organics in the nucleation process or gas-phase oxidation, it is difficult to understand how significant amount of organics would condense onto/into a non-absorbing inorganic phase under sub-saturated conditions and the absence of any chemical reaction.

Our current hypothesis is that much of this uptake on neutral particles is simply due to solubility of polar gases, as was demonstrated in the experiments of Li et al., 2011. Even under sub saturated conditions, polar gases will partition to a wet particle. We have clarified this mechanism throughout the manuscript as discussed in our response to the specific points (1-5) below. Although one can not fully prove or disprove such a mechanism, the fact that experimental observations, such as organic spectra and SO4 mass (volume) correlation agree very well with Li et al., 2011 indicates that this is likely, since solubility was the dominant cause of uptake in that study for particles containing water, and the particles in the current study also likely contained water.

Their observations are particularly hard to reconcile with the fact that these gases apparently didn't partition to the ambient sulfate and organic aerosol (at least at significant levels) despite being more concentrated in the ambient air and with the fact that the gases that condensed in the experiments are less oxygenated and presumably more volatile than the ambient OA. The authors should propose some mechanism, similar to what is presented for the acidic seed experiments, to explain their observations.

We did not say whether these gases partitioned to ambient particles or not. It is not possible to if these gases partitioned in the atmosphere, especially in the presence of the multitude of other processes occurring in the ambient atmosphere which also lead to OA. The apparent non-partitioning in the real atmosphere pointed out by the reviewer may have been the end results of prior partitioning. We are not convinced that the apparent non-partitioning is a foregone conclusion, or truly a fact, since no one has any idea of the VOC interaction history of an atmospheric sulfate aerosol. The partitioning process, as revealed here and in the previous study by Li et al. (2011), is fast, and under ambient conditions it is difficult to detect and measure with ambient measurements of aerosols. Thus the apparent non-partitioning in the real atmosphere does not negate the current experimental results.

We also did not say that the gases were more concentrated in the ambient air. Since we used ambient air for these experiments, the concentration of gases should be the same inside the chamber and in the ambient air. One must also keep in mind that the seed aerosol used in these experiments is quite different than the ambient aerosol likely present, in that we are using fresh sulfate. This should be considered as representing a starting point for atmospheric sulfate aerosols before they interact with organic vapors. Furthermore, it is not clear if partitioning of these gases would occur on a sulfate particle containing/coated with some other pre-existing organics. However the referee's point is well taken in that a potential mechanism would be very helpful for reconciling results. We have modified the manuscript by adding a paragraph discussing the phase of particles and the potential mechanism for neutral experiments. This is outlined in the responses below.

Below are further suggestions for revisions the authors could make to the manuscript which would help understand the uptake mechanism and strengthen their assertion that uptake of primary organic gases onto neutral seed is an important atmospheric process.

1) The authors should include a discussion of the seed phase. The acidic seed particles are clearly liquid, but the phase of the neutral seed is ambiguous. Based on the reported CE (.22 in some experiments) and the RH, I infer that the seed is solid. However, if the reported RH's are sometimes above the efflorescence point so it is possible the seed is a metastable liquid if it initially formed as a liquid. The phase is relevant as it is very difficult to understand how dry, essentially unreactive inorganic seed particles would uptake organics in the absence of any reaction. If however, the particles were in a metastable state, I can see hygroscopic gases dissolving into the aqueous layer, though timescale seems wrong (see below).

We agree that the phase of the particle is important, and have included discussion of this point in the revised manuscript. The RH (40-50%) was always above the efflorescence point for ammonium sulfate (30-35%), and the particles always started out as liquid particles. The CE for the AMS was consistently above 0.22 except for one experiment (E12). (Unfortunately we cannot explain why the CE for this one experiment was so low, but given the difficulties associated with determining the CE in the first place we suspect there is considerable uncertainty in this and all other CE values.) Given that they were wet particles, we believe that the mechanism of uptake under neutral conditions is likely a simple solubility, as was demonstrated in Li et al 2011. A relationship between particle volume (as opposed to surface area) and organic uptake in Li et al., 2011 has demonstrated this fact. A similar relationship in this study implies a similar mechanism. We have now stated these points more clearly in the manuscript which now reads as:

"Several factors suggest that the mechanism of organic uptake under these neutral (and near neutral) conditions is likely the dissolution of primary polar gases to a partially aqueous aerosol. Firstly, as was demonstrated in Li et al 2011 a relationship between seed particle volume (as opposed to surface area) and organic mass uptake for aqueous particles implied a solubility mechanism. Similar organic aerosol spectra and seed particle volume dependence in the current study compared to that of Li et al., 2011 suggests a similar mechanism. This is also consistent with the fact that the neutral particles in this study began as liquid droplets, and likely contained significant water after neutralization since the chamber RH (40 – 50%) was significantly above the efflorescence RH of ammonium sulfate (30-35%; Smith et al;., 2012)."

2) The authors should comment on organic uptake timescales since it provided important clues into the uptake mechanism. The timescale (<2 minutes) indicates that the equilibration time is extremely fast, faster even than the timescales that would be required mixing processes. It is also difficult to imagine any condensed-phase reaction process coming to completion on this rapid a timescale. How long did it take for the formation of sulfate seed to come to completion? Is it on the same timescale?

We agree that the timescale of uptake in these experiments is an indeed important point. The timescale for SO4 formation is very fast; although coagulation of these SO4 particles takes somewhat longer (< a few minutes). Regardless, since we are normalizing the organics by the sulfate mass, the fast organic equilibrium remains valid. The fact that organic equilibrium is reached so rapidly, implies that it is indeed a solubility mechanism for polar organics.

We also agree that a condensed phase reaction mechanism coming to completion so quickly is difficult to imagine. This is consistent with the fact that for acidic experiments where there is reaction, such an equilibrium takes hours (if at all) to be established. The fast equilibrium for neutral experiments (ie: without reaction) with liquid particles, is in part what suggests a solubility mechanism. This rapid equilibrium remains consistent with Henry law solubility, regardless if gas-particle diffusion or gas-interface transport is the rate limiting step, as can be demonstrated with the characteristic times for such processes, derived via the equations of Shi et al., 1991 and others and summarized in Seinfeld and Pandis (1998). These processes, according to these equations results in an equilibrium achieved on the order of a milliseconds to seconds in a closed system. We have more clearly discussed the timescale and its implications in the manuscript in an additional paragraph which reads*:*

"Finally, the equilibrium timescale for organic uptake under these conditions was less than approximately 2 minutes (Figure 1A). This rapid equilibrium is consistent with Henry law solubility, where gas-particle diffusion or gas-interface transport is the rate limiting step. As demonstrated by Shi et al., 1991 and summarized in Seinfeld and Pandis (1998) the characteristic time for such processes results in an equilibrium achieved on the order of milliseconds to seconds in a closed system. Conversely, equilibrium in a reactive system may take significantly longer (ie: Figure 1B) potentially due to slow liquid phase chemistry, or mass transfer limitations caused by the increased organic mass added in acidic experiments resulting in changes in the organic aerosol viscosity (Vaden et al., 2011; Perraud et al. 2012)"

3) The manuscript would benefit from showing data before injection of the SO3 gas. Showing the data before injection of the SO3 gas would allow readers to assess the instrument's ability to measure a zero and visualize the organic deposition timescale. It would also help understand the timing of the NH3 and SO3 injections.

We agree that data before SO3 injection would be beneficial. Unfortunately, prior to the addition of SO3, the AMS was sampling ambient air as noted in the caption of Table 2. The addition of SO3 and valve switching to the chamber occurred at approximately the same time. However a reasonable estimate of the zero value is presented in Figure 1B, for the case where no organics are present.

4) Please state the length of time between injection of the ammonium gas and the SO3 gas. Do the reviewers notice organic formation from ammonium addition alone?

Can the authors comment on the possibility that he large excess of ammonia gas is driving the organic condensation? Is possible that the large excess of ammonia gas is reacting with alkanoic acids to form salts? The authors state that amine formation was not observed in the gas phase, but they could partition rapidly to the condensed phase. Was significant nitrogen observed in particle-phase?

The ammonia gas in all experiments was present before any SO3 (and hence particles) was added. Therefore, the time between SO3 and NH3 is not relevant. However, we have clarified the text in this regard which now reads as:

"Ammonia (NH_3) was always present (or added) in the chamber prior to SO_3 addition, at levels that ranged from ~ 1 – 43 ppbv"

We did observe nitrogen containing fragments in the organic aerosol spectra, but these are primarily during the highly acidic experiments. In those experiments we think it is more likely that carbonyls react with ammonia or amines to form imines via the acid catalyzed mechanism of Wang et al., 2010. Regardless it is likely not the dominant organic formation mechanism under acidic conditions and certainly not important under neutral conditions. We have added text to address this possibility and included an additional high resolution spectrum (fig 5C) showing the nitrogen fragments. The relevant text in section 3.2.1now reads as:

"Equations (1) and (2) are also the first steps to other reactions leading to oligomeric compounds such aldol, acetal, imine and cationic polymerization products (Noziere et al 2003; Liggio et al., 2007; Wang et al., 2010) some of which are not formed through reversible reactions or require an acid catalyst in the forward and reverse directions. The formation of products from irreversible reactions would also slow theeventual shift in equilibrium back to the starting olefin (Eq 1) via ambient ozonolysis reaction (eg: Morris et al. 2002). Indeed, under acidic conditions a number of nitrogen containing fragments were observed in the organic aerosol spectra, as depicted in Fig 5B, possibly as a result of acid catalyzed irreversible imine formation reactions (Wang et al., 2010)."

5) Can the authors observe any changes in the PTR-MS concentrations when organic uptake/condensation occurs? Are there any clues from the PTR-MS about what species are partitioning to the condensed phase?

The PTR-MS is not sensitive enough to observe such small changes in the gas phase resulting from the uptake of gases, particularly under neutral conditions where the uptake is smallest. This was stated on pg 29076 lines 22-25.

My other major comment is in regard to the terminology the reviewers use to describe the OA. In the abstract and in the conclusions, the authors seem to assert that the organics formed are primary organic aerosol (e.g., P 29083, lines 12-16). In the case of uptake onto the acidic seed aerosol, this is clearly not the case as heterogeneous chemistry drives uptake. I would argue that the OA should be classified as secondary because the primary gases undergo chemical transformation. In the case of the neutral seed experiments, the terminology is more ambiguous until the mechanism is constrained. Ordinarily I would consider this a minor and somewhat pedantic point, but the authors ascribe significant importance to the distinction between POA and SOA in the manuscript, so they should clarify the language.

We agree that the organics for highly acidic particles should not be considered primary since there was chemical reaction occurring and driving the uptake. This was not our intent, but we can see how this could be interpreted from the wording. We have clarified this point in the abstract and conclusions by more clearly making the distinction between experiments and results. The relevant parts of the abstract now reads:

"For non-acidic seed aerosol the uptake was attributed to the direct dissolution of primary vehicle exhaust gases into the aqueous aerosol fraction, and was correlated to the initial seed sulphate mass. The uptake of primary oxygenated organic gases to aerosols in this study represents a significant amount of organic aerosol (OA) that be considered primary when…." "These two processes, forming oxygenated POA under neutral conditions and SOA under acidic conditions can contribute to the total ambient OA mass and the evolution of ambient aerosol O:C ratios."

and the conclusion section has been modified to read:

"The present results have several different implications for ambient organic OA mass and composition in the presence of either neutral or acidic aerosol. Foremost, they imply that the dissolution of gasoline exhaust vapours onto pre-existing neutral seed mass as demonstrated previously (Li et al., 2011), will occur under ambient….."

"….However, under neutral conditions assuming a simple solubility mechanism for primary gases, this uptake should be considered to be primary. Thus this dissolution of primary polar organics represents a significant amount of POA compared….."

"Conversely, organic mass uptake in the present study, utilizing the ambient mixture and concentration of gases is greatly enhanced under acidic conditions, due to aerosol-phase reactions forming products which are more oxygenated than dissolved species on neutral aerosols. In this case, the reactive uptake facilitated by acidity should be considered an additional source of SOA, since both primary and secondary gases are transformed to other products within the aerosol."

For neutral seed particles, given the solubility mechanism, and similarity to organics from engine exhaust experiments we continue to believe that these should be considered primary. However, we have more clearly made the distinction between the two types of experiments and associated uptake mechanisms as noted above.

Minor Comments and Technical Corrections

Can the authors comment on the neutralization of the seed? The observed ammonium: sulfate ratios are significantly below 2 in many of the experiments despite the large excess of ammonia in the gas phase. The measured ratios in some experiments (E4, E8, E14) appear to deviate from the expected value by a factor larger than experimental error.

We agree that the some experiments remain acidic despite high ammonia in the gas-phase. This is consistent with previous experiments which demonstrate that neutralization in the presence of organics is not always as fast as theoretically expected (Liggio et al., 2011). We have therefore regrouped the experiments into a third group which include those which are slightly acidic based on the NH4/SO4 ratio (E4, E8, E14). Also see responses to reviewer #1. Regardless, slightly acidic experiments behave much like fully neutral experiments, and do not affect the conclusions of the paper. We have added text to note these points:

"In some experiments particles remain slightly acidic despite an excess of NH_3, consistent with a reduced NH_3 uptake in the presence of organics as demonstrated in Liggio et al., 2011."

The text annotations within figures 2, 3, and 6 are small and difficult to read when printed.

We have fixed this issue.

Tables 1 and 2 – Separating the control, acidic seed, and neutral seed experiments with a line and a label (like is done to separate the control experiments from the rest in T2) would make it easier for the reader to understand the data.

We have made this suggested correction

Table 2. Can the authors also list the final organic concentrations? It would be particularly useful for the acidic seed experiments where significant uptake after 2 minutes is observed.

We can include the final organic concentration, however due to large particle wall loses, the final concentration is not very meaningful. What is more meaningful is the final organic/SO4 ratio (which normalizes out wall loses). This is indeed shown in Table 2.

Page 29071, lines 15-20. Kroll et al. (2011) should be cited. Kroll, J. H., Donahue, N. M., Jimenez, J. L., Kessler, S. H., Canagaratna, M. R., Wilson, K. R., Altieri, K. E., Mazzoleni, L. R., Wozniak, A. S., Bluhm, H., Mysak, E. R., Smith, J. D., Kolb, C. E., and Worsnop, D. R.: Carbon oxidation state as a metric for describing the chemistry of atmospheric organic aerosol, Nat. Chem., 3, 133-139, 10.1038/nchem.948, 2011.

We have now cited the paper.

The authors' observations also have implications for other chamber experiments. Many chamber SOA experiments employ dry AS seed particles, and none that I am aware of have reported organic uptake before an oxidant was introduced, though the precursor gases are admittedly different. However, crystalline AS seed is generally believed to be inert in these experiments and the processes the authors identify could affect chamber experiment employing AS seed once oxidation is initiated. The authors may want to comment on this potential artifact.

We do not believe that the particles were dry in this case, and thus we cannot say what implications these experiments could have on dry chamber experiments elsewhere. However, for other chamber experiments with wet seeds, uptake of polar gases could indeed be an issue.

Did the authors take any steps to remove oxidants present in the ambient air from being injected to the chamber? Can the authors comment on oxidant levels? I would expect that some ozone would have passed through the filters and made it into the chamber.

Indeed, some ozone may have been in the chamber. However, we believe this concentration to be rather low due to NO titration, given the close proximity of the lab to the roadway (<100 m). Regardless ozone oxidation is too slow to explain how organic mass is added and reaches equilibrium on such a short timescale in neutral experiments. In acidic experiments, the mass added via liquid phase reactions was much higher in a short time than could be expected via ozone chemistry. We have added text to manuscript (section 3.2.2) to note these points:

"Increases in O:C over time, possibly due to oxidative chemistry in the dark (ie: O_3 and NO_3) are not likely, since a large and evolving organic mass and O:C was only observed for acidic aerosol experiments, while ozone was likely present in small amounts during all experiments. Regardless, ozone chemistry forming SOA is likely too slow to form the large amount of organic mass observed here on such a short time scale (both in acidic and neutral experiments)."

Reviewer #3

General Comments:

In this study the authors investigated the uptake of primary oxygenated VOCs onto acidic and neutralized sulfate particles. The experiments were conducted by exposing filtered urban ambient air to sulfate particles and measuring the addition of organic matter to the seeds using an aerosol mass spectrometer. Comparison of mass spectra and O/C ratios with previous studies indicate that the uptake was probably due to oxygenated VOCs directly emitted from vehicles. For the most acidic seed, organic growth appeared to be due in large part to oligomers formed from acid-catalyzed reactions of carbonyls. The study is an interesting one and suggests that future studies should consider the possibility that primary oxygenated VOCs can directly form aerosol, making it more difficult to determine the relative importance of SOA and POA to oxidized organic aerosol. I think the paper is suitable for publication in ACP after the following comments/questions have been addressed.

Specific Comments:

1. Page 29079, lines 3–6: Are these carbonyl measurements relative to total primary organic mass or the amount resolved by the analytical techniques?

These are relative to the total primary organic mass as determined via typical OC/EC measurements

2. Page 29080, lines 17–24: How is it known that there is less water available for hydration after adding NH3? Studies by Zhou et al. (2006) Env. Sci. Technol., 40, 7682, have shown for example that sulfuric acid reduces hydration of methylglyoxal, so perhaps in this case neutralizing the acid makes water more available for hydration. Might the evaporation of OA be caused by the formation of solid ammonium sulfate, thus eliminating some of the sulfuric acid/water liquid phase into which organics were dissolved?

We agree that we cannot know for certain that that there is less water available for hydration after neutralization. However, thermodynamics dictates that if equilibrium is re-established, the particle should have less water than before, although it is possible that the remaining water is more "available". We do not believe that we made solid ammonium sulfate, but certainly the loss of some water could result in a loss of OA (ie: less to dissolve in) as the reviewer suggests. We have included this point in the manuscript which now reads:

"It may also be possible that the neutralization of the aerosol results in OA evaporation which accompanies the loss of sulphuric acid/water liquid phase that the OA was dissolved in. Given the evidence for reactive uptake in acidic particles, simple OA evaporation is less likely. "

3. Page 29081: Shouldn't the products of reactions (1) and (2) be R-CH-C(OH)-R and

R-C(OH)2-R, respectively?

For simplicity we had not included hydrogen atoms in eq 1, but have now included them as suggested. We thank the reviewer for noticing the error in Eq 2. It has now been corrected.

4. Page 29081: The occurrence of reaction (1) to any significant extent in ambient aerosol seems unlikely. In liquid particles in which such a reaction would occur, ozone would have easy access to the alkene C=C bond and so rapidly remove the alkenes as the equilibrium continued to shift to the left. Many studies of the heterogeneous kinetics of alkenes in particles (e.g., Morris et al. (2002) Geophys. Res. Lett., 29, 71-1–71-4), typically liquid oleic acid, have shown that the reaction is sufficiently fast that in the atmosphere the lifetime of alkenes in liquid particles will be only a few minutes. Only when alkenes are in solid or glassy particles, which would presumably preclude the occurrence of reaction (1), are they inaccessible to ozone and so stable for longer periods of time.

We agree with the reviewer in that alkenes are available for ozonolysis in the ambient atmosphere, which could remove them from the particle phase over time if equilibrium shifts to the left in eq 1. However, as mentioned on pg 29081 lines 4-5; equation 1 is also the first step to the formation of other oligomeric compounds which may not be reversible. We have noted the reviewers point in the text which now reads:

"The formation of irreversible products would avoid the slow but eventual shift in equilibrium back to the starting olefin (Eq 1) via ambient ozonolysis reaction (eg: Morris et al. 2002).".

5. Page 29081, lines 3-5: I've never seen it suggested that aldol condensation and acetal formation are irreversible (I don't know about cationic polymerizations). It may take a while for oligomers that are formed by these reactions to dissociate, monomer by-monomer, but I think this is possible.

We agree with the reviewer that aldol condensation and acetal formation are generally reversible. The exception may be the dehydration of aldol products which can also be promoted under the same acidic conditions. The other possibility is the reaction of carbonyls under acidic conditions with ammonia and/or amines to form imine products irreversibly. We have corrected and clarified the text which now reads:

"Equations (1) and (2) are also the first steps to other reactions leading to oligomeric compounds such aldol, acetal, imine and cationic polymerization products (Noziere et al 2003; Liggio et al., 2007; Wang et al., 2010) some of which are not formed through reversible reactions or require an acid catalyst in the forward and reverse directions. The formation of products from irreversible reactions would also avoid the slow but eventual shift in equilibrium back to the starting olefin (Eq 1) via ambient ozonolysis reaction (eg: Morris et al. 2002). Indeed, under acidic conditions a number of nitrogen containing fragments were

observed in the organic aerosol spectra, as depicted in Fig 5B, possibly as a result of acid catalyzed irreversible imine formation reactions (Wang et al., 2010). The irreversible formation of these and other products may explain why the oligomerization products, as represented by (m/z >300)/SO_4 in Figure 1B do not decrease upon addition of NH_3 and subsequent aerosol neutralization. However, even reversibly formed oligomers are likely stable in the absence of an acid catalyst."

6. Page 29081, lines 6–8: It seems like perhaps the reason the oligomers did not dissociate to monomers after adding NH3 is not because the reactions are inherently irreversible, but that the acid needed to catalyze the reverse reactions had been neutralized. Catalysts are necessary for both forward and reverse reactions, so once oligomers are formed they should be stable in the absence of the catalyst. This is not necessarily the case for hemiacetals, however, since they can generally be formed with little or no strong acid present.

We thank the reviewer for this important point. This is a very likely possibility and has now been included in the text: (see one response previous for text)

7. Page 29083: Considering the proposed importance of uptake of oxygenated primary VOC emissions to OA formation, do the authors know of any estimates of the ratios of volatile VOC reaction products relative to oxygenated primary VOCs in urban air? Unless there is something special about uptake of primary oxygenated emissions one would imagine that reaction products of most VOCs would be taken up similarly or probably more efficiently since they are often more highly oxygenated. It would be interesting to use this ratio to estimate the contribution of the uptake of volatile VOC reaction products to OA by multiplying it by the value of 0.14 ug/m3 estimated for primary oxygenated VOCs.

It is difficult to determine what such a ratio would be in ambient air. We are not aware of any literature that reports such a value. We do agree that this could be a possibility, and have now noted this point in the implications section (4.0):

"In principle, the dissolution of secondary oxygenated VOCs into an aqueous sulphate aerosol is also possible, and perhaps more important given their tendency to be more highly oxygenated.".

However, to make such a quantitative calculation would be highly speculative and beyond the scope of this paper.

8. Table 2: The PM ratios of Org/SO4 used here are high compared to the atmosphere. How might this affect the results of the experiments?

With the exception of E1 (0.75), all the experiments are either in line with ambient observations (Zhang et al 2007) or even lower than in the ambient atmosphere. We do not believe this will have an effect on the results.

Technical Comments:

1. Page 29075, line 20: I think this is supposed to be "41, 43, 44, 55,. . ."

We have made this correction

2. Page 29079, line 20: "Aerosol" should be "aerosol".

We have made this correction

3. In a number of places the authors have written m/z 300/SO4 instead of m/z > 300/SO4.

We have made this correction

4. Throughout the paper the authors refer to "reversible or irreversible products". I take this to be shorthand for "products formed by reversible or irreversible reactions", but I think the discussion would be clearer if the authors rewrote this text referring to reactions as reversible or irreversible and not products.

We have made the suggested changes throughout.

References:

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Seinfeld, J. and Pandis, S., Atmospheric Chemistry and Physics - From Air Pollution to Climate Change, John Wiley & Sons Incorporated, New York, 1998.

Shi, B., & Seinfeld, J. H. On mass transport limitation to the rate of reaction of gases in liquid droplets. Atmos. Environ., *25 A*(10), 2371-2383, 1991.

Smith, M. L., Bertram, A. K., & Martin, S. T., Deliquescence, efflorescence, and phase miscibility of mixed particles of ammonium sulfate and isoprene-derived secondary organic material. Atmos. Chem. Phys., *12*(20), 9613-9628, 2012.