Response to reviewers for Allen, et al., “Influence of crustal dust and sea spray supermicron particle concentrations and acidity on inorganic NO_3^- aerosol during the 2013 Southern Oxidant and Aerosol Study,” 2015.

We thank both of the reviewers for their constructive comments on the manuscript. We have taken these suggestions into full consideration and we believe they have helped improve the quality of the final revised paper. Our replies (in non-italics) to specific comments and concerns (italicized) are given below.

Comments from referee #1

General Comments

This study describes the results of gas and aerosol sampling in the southeastern U.S. during the SOAS campaign. The focus is on aerosol nitrate and its occurrence during several mineral dust/sea salt events. I think that overall, this work is highly novel and will be of interest to many in the atmospheric chemistry community. Among their findings, those that stood out as particularly interesting were: 1) the importance of dust and sea salt in the southeastern US – a region not typically thought of as having high contributions from either source, and 2) the observation that differences in measured aerosol nitrate concentrations between techniques may be influenced by minor differences in the cut point sample inlets due to the presence of nitrate in the coarse mode. The second point, especially, seems quite novel (at least to this reviewer), although the authors do not give it a great deal of discussion. I think with a little more analysis, this could have more substance (for example, comparison of their MARGA nitrate measurements ($PM_{2.5}$) to AMS nitrate (PM_1) measurements).

These plaudits aside, there are some issues with the article that need to be addressed before it is suitable for publication in ACP. These are detailed in both sections below:

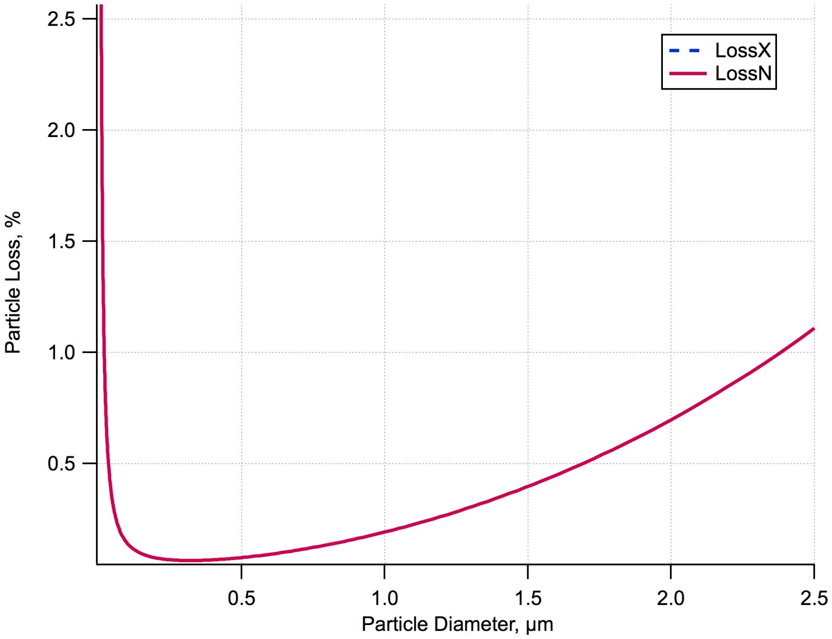
Specific Comments

1. I have two concerns with the sampling methodology used for the MARGA system. First, why were two cyclones deployed in series? I am not familiar with such a sampling configuration. Cyclones can have a relatively high pressure drop, so I wonder if this could affect the cut point efficiency of the second cyclone? Are the results in Figure S6 taken with both cyclones deployed?

This sampling arrangement was done simply because the primary rooftop upper inlet was a PM_{10} “hat”. We expect that this first inlet had minimal pressure drop, and mainly served to avoid the intake of rain or bugs to the system. The downstream $PM_{2.5}$ inlet was thus the actual determinant of the instrument size cut. However, we acknowledge that this configuration may have affected the cut point efficiency of the second cyclone and have added a note to this effect in the relevant discussion in the supplemental information. The results in Fig. S6 (now Fig. S7) were not taken with both cyclones deployed.

2. My second concern is more significant: pg. 13833 ln 25-26 describes a 1.5 m segment of polyethylene tubing used for the MARGA sample inlet line. I would expect this material to cause significant particle losses in this segment of the sample line. Did the authors consider this effect, and if so, what was the magnitude/impact on the aerosol measurements?

We estimate the losses in the polyethylene tubing to be small due to the high sampling flow rate. Hypothetical losses for gases (HNO_3 as a representative example) due to sampling through this line were calculated using the method suggested in Trebs et al, 2004.[1] Using eq. 2 in the reference, and assuming that HNO_3 has an uptake coefficient of 0.05 on liquid H_2O surfaces[2], the estimated loss of HNO_3 due to this tubing is around 3%. In addition, polyethylene has been found to have a low affinity to adsorb HNO_3 vapor.[1] In regards to aerosol losses: using an inlet loss calculator[3] shows that, at the high sampling rate, the losses are less than 1.5% for particles between 0.25 and 2.5 μm (see figure below).

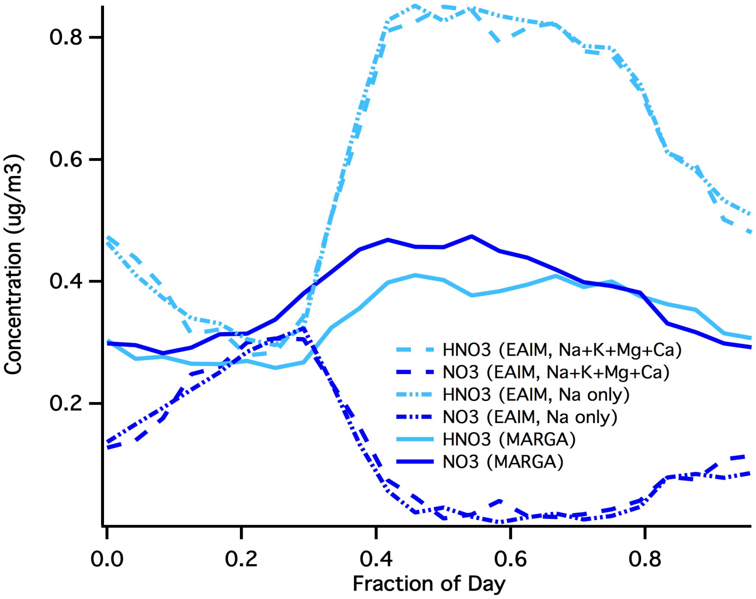


[1] Trebs et al., *Atmos. Chem. Phys.,* 4, 967-987, 2004.
[2] Value of 0.05 was taken from Sander, S. P., et al., "Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation No. 17," JPL Publication 10-6, JPL, Pasadena, 2011 http://jpldataeval.jpl.nasa.gov.
[3] von der Weiden, et al., Atmos. Meas. Tech., 2, 479-494, 2009.

3. I have two questions about the inorganic modeling (Section 3.6):
a. for the E-AIM simulations, how were the components not included by the model accounted for? If the calcium/magnesium/potassium equivalents were input as H^+ *(to meet the model's requirement of charge balance on input), I would expect that to have a very different impact on predicted nitrate than the same simulations treating crustals as equivalent sodium, as other studies have done. This may help to explain the significant*

difference in E-AIM predictions of aerosol nitrate.

The model was originally employed with only concentrations of Na^+, with Ca^{2+}, Mg^{2+}, and K^+ equivalents input as H^+. We have since reviewed how the E-AIM model was originally implemented and have corrected some of the inputs. The results of the new model run (shown in Fig 7 and corresponding text) now include Ca^{2+}, Mg^{2+}, and K^+ as equivalent Na^+. However, in general we observe that because the majority of the mineral species concentrations was from Na^+, the difference between including Ca^{2+}, Mg^{2+}, and K^+ as H^+ equivalents or as Na^+ equivalents is minimal (see figure below).



b. Perhaps I am just misinterpreting Figure 7d, but there seems to be a major disconnect with the E-AIM model results. The total (HNO_3 + NO_3-) measured nitrate concentration appears to be significantly higher than the total modeled nitrate concentration. Even if E-AIM is partitioning a disproportionate fraction to the gas phase, why is there not a material balance on HNO_3 + NO_3^-? Note, for ISORROPIA, the total modeled and measured nitrate appear to be quite similar.

We thank the reviewer for pointing out this discrepancy. Upon reviewing how the E-AIM model was implemented, we discovered that nitrate had been added into the model as only NO_3^-, rather than the sum of NO_3^-+HNO_3. We have corrected this error and rerun the model. The results of the new model run, which now shows mass conservation, are presented in Fig 7 and the text of the corresponding section (Section 3.6) has been corrected in light of these new results.

*4. In Section 3.5, the authors support their claim for nitrate production on the surface of the dust particles by noting that the rate of HNO_3 uptake is controlled by the enhanced surface area contributed by the larger particles. However, the authors should also discuss how the *rate* shown in Figure 6d connects to the observed aerosol nitrate concentration in Figure 6a. Further, the authors state that "higher rates of aerosol NO_3^- production track more closely with higher Sa than with other factors that contribute to*

NO_3^-" – this would be supported by showing gas-phase NH_3 data. Similarly, in the instances where the authors suggest chloride displacement was the major route for HNO_3 uptake – e.g., Section 3.3 – the argument would be strengthened by showing and discussing the MARGA HCl data.

We agree with the reviewer's suggestion. We have added a panel depicting SO_4^{2-} concentrations to Fig 6, as we believe this is the most salient other factor that may have affected NO_3^- formation (due to the influence of SO_4^{2-} on aerosol acidity, as higher SO_4^{2-} means more acidic aerosol and thus more condensation of HNO_3 into the aerosol phase). We have added brief discussion comparing the predicted rate of NO_3^- formation with the observed NO_3^- concentrations to the relevant section (pages 13845, line 18 to 13846, line 4). In addition, we have added gas phase HCl concentrations measured by MARGA to Fig. 3b, and included consideration of HCl data when discussing chloride displacement as a possible route for HNO_3 uptake.

5. Pg. 13844, line 16-19: there are many instances throughout the paper (this sentence is one example) where the authors need to be more careful with their notation. This sentence gives the impression that 'coarse mode particles' is applied to PM > 1 μm.

We thank the reviewer for pointing out this discrepancy. We have altered the text (including the indicated sentence) to clarify when we mean supermicron particles (PM > 1 μm) and when we mean coarse mode particles (PM > 2.5 μm).

6. Pg. 13831, line 6: in 'highly acidic environments' with excess sulfate, I would not say that the NH_4NO_3 dissociates, as much as the limited NH_3 preferentially associates with sulfate, leaving HNO_3 in the gas phase.

This portion of the text has been altered to better reflect some of the underlying thermodynamic processes involved. For example, the phrase the reviewer highlights here as been changed to "Addition of acidic H_2SO_4 to the aerosol system, as occurs in environments dominated by SO_2 pollution, will drive NH_3 condensation into and HNO_3 evaporation from the particles as the aerosol system reestablishes a new thermodynamic equilibrium. The NH_3 driven into the particle phase will associate with sulfate, leaving HNO_3 in the gas phase."

7. Pg. 13832, line 2-3; Pg. 13841, line 6-9: the authors are referred to other studies which suggest much longer equilibration timescales than the authors assume here. For example, Fridlind and Jacobson (JGR, 2000) model HNO_3 equilibration timescales with 2-3 μm sea salt particles that are ~5-20 hours, with considerable variation dependent on α.

We thank the reviewer for highlighting this discrepancy. The text on page 13832 lines 1-6 and page 13841, lines 6-9 has been changed to more accurately reflect the available literature on aerosol partitioning times. The equilibrium partitioning times for HNO_3 on sea salt particles has been corrected from "on the order of minutes" to "on the order of 5 to 20 hours" with updated references.

8. Section 3.4: the discussion in this section gives the impression that all particles/particle types were externally mixed? Is that the case?

No, particles were not only externally mixed and were mostly mixtures of different sources with different secondary species, which will be discussed in an upcoming publication. The section and figure focus on labeling the source (or labeled as secondary if formed in atmosphere) to simplify the representation. This point has been clarified in the text.

9. Pg. 13846, line21-23: what is meant by this sentence?

This sentence has been removed from the text. The associated discussion has been clarified to indicate that we consider E-AIM to have too strong of a reliance upon temperature-driven phase partitioning of HNO_3 and NO_3^-, rather than considering all the factors that might contribute to HNO_3/NO_3^- partitioning (such as mineral species).

Technical Corrections

1. Abstract, line 3-4: suggest removing "1 June to 15 July"

Dates removed from this line in the abstract.

2. Abstract, line 5-7: suggest removing "an ion chromatograph coupled with a wet rotating denuder and a steam-jet aerosol collector for monitoring of ambient inorganic gas and aerosol species"

Text removed from abstract.

3. Pg. 13830, line 6: what is meant by 'a dominant pollutant'?

By "dominant pollutant" we meant that NO_x is expected to become one of the most prevalent pollutants in the near future (even more so than currently as SO_2 concentrations rapidly decrease due to tighter emissions controls). This phrase has been changed in the text.

4. Pg. 13830, line 7-8: run-on sentence

Pg. 13830 line 7-8 has been broken into two sentences.

5. Pg. 13830, line 10: I would say regulators or regulatory agencies are also quite interested.

We agree with this point and have added this observation to the text.

6. Pg. 13830, line 23: Temperature and aerosol water also strongly affect aerosol *nitrate concentrations.*

This observation has been added to pg 13830, line 23 of the text.

7. Pg. 13832, line 12: change 'a glimpse' to 'insight'

Text has been changed.

8. Pg. 13834, line 18: say 'chemical suppressor' instead of 'suppressor ion exchange columns'

Text has been changed.

9. Pg. 13835, line 24: do the authors mean 'biomass burning'?

Yes, the authors mean biomass burning and have changed this in the text, as well as in the figure legend.

10. Section 2.2.2: give the range of particle size analyzed by this method

Particles from 0.1 – 10 μm were analyzed (the lower limit is based on our analysis method, CCSEM-EDX). This point has been added to Section 2.2.2 of the text.

11. Note that Guo et al. (2014) reference is now an ACP article

Reference has been updated.

12. Pg. 13839, line 26: note that the cited values from Guo et al. are modeled using ISORROPIA, not 'measured'.

Text has been clarified.

13. Pg. 13840, line 1-2: say 'inorganic ionic species'

Text has been changed to read "inorganic ionic species."

14. Pg. 13840, line 26: see Specific Comment #5 above

This and other instances of "coarse mode" have been changed to "supermicron" when referring to particles PM>1 μm.

15. Pg. 13841, line 21: change 'suggest' to 'suggests'

Text has been changed.

16. Pg. 13842, line 3-5: are the fractions (45.2% and 41.8%) statistically different?

Error analysis reveals that the fractions for the percent of minerals composed of Si (45.2% and 41.8% during the two coarse particle events, respectively) are not statistically different. These values have been removed from the discussion of the differences in composition between the two coarse particle events in Section 3.3 of the text. The numbers remain in Table 2, but with percentages reported to the tens place to make clearer the precision of these numbers.

Comments from referee #2

General Comments

This manuscript reports an analysis of factors that control the gas-aerosol phase partitioning of HNO_3 in the southeastern US during the SOAS campaign. The topic is relevant for publication in ACP, the measurements by a new-generation instrument are interesting, and the interpretation involves state-of-the-science tools including FLEXPART retroplumes and thermodynamic models.

The authors measurements indicate that periods during which particulate NO_3^- concentrations were higher relative to other periods were associated with concentrations of marine aerosols and/or crustal dust that were also relatively high. These results are relevant to understanding of regional air quality. However, as summarized below and described in more detail under the specific comments, explicit quantitative evaluation of the underlying multiphase processes as well as interpretation of associated implications for regional air quality are constrained by several factors.

- *Based on information reported in the manuscript, the reliability of the HNO_3 and particulate NO_3^- measurements on which the analysis focuses is highly uncertain. Comparisons with results from co-located instruments, post-campaign evaluations of performance, and the authors' own data are significantly biased by large amounts and, thus, the utility of their interpretation is problematic.*

We understand the reviewer concerns regarding the differences in gaseous HNO_3 and particulate NO_3^- measurements. In regards to the differences in NO_3^-, we believe the main difference between the instruments is due to the different efficiencies of the $PM_{2.5}$ size cut. Additional comparisons to NO_3^- measurements at the SOAS site, an AMS with a PM_1 size cut operated by a group from the University of Colorado, Boulder and filter pack samples from the EPA's IMPROVE network, support this conclusion. The additional datasets and subsequent discussion have been added to the supplemental information. We continue to believe that wall effects within the long MARGA inlet may account for the discrepancies in three available HNO_3 measurements. We also note that the discrepancies in HNO_3 concentrations do not alter our final conclusions about uptake rate, as discussed in the supplemental material. Further discussion of the reviewer's concerns about the differences in NO_3^- and HNO_3 is given below under the relevant specific comments.

- *The aerosol data correspond to nominal $PM_{2.5}$ sampled in bulk. Because the chemical processes of interest with respect to HNO_3 phase partition and cycling vary as a function of size-resolved particle composition and acidity, thermodynamic evaluations based on bulk $PM_{2.5}$ may have little if any direct relevance to the corresponding processes in ambient air.*

Given the importance of aerosol size in our analysis, we acknowledge that a lack of size-resolved particle composition and acidity means we cannot determine the full impact of mineral aerosol on HNO_3 cycling. However, we believe that the fact that we observe enhanced particulate NO_3^- during periods of higher mineral and sea salt supermicron aerosol (as monitored in bulk $PM_{2.5}$) is evidence that this bulk composition is predictive of HNO_3 uptake.

- *In addition, the authors' analysis suggests that much of the aerosol mass and NO_3^- was associated with particles greater than 2.5-µm ambient diameter, which were not sampled (or were sampled at unknown efficiency). Consequently, the full impact of marine and/or crustal aerosol on HNO_3 cycling cannot be evaluated based on the reported results.*

We agree with this limitation of our analysis, and have added comments to the manuscript suggesting that because the coarse mode NO_3^- is under-measured, the actual contribution of this process to aerosol-phase NO_3^- may be larger than in situ $PM_{2.5}$ measurements would suggest. However, we note that for the prediction of the uptake rate, we do have measurements of the full aerosol surface area size distribution so we would not necessarily be underestimating the relative importance of that process.

- *Results for the E-AIM model indicate that mass was not conserved, which implies that the model was improperly implemented. Consequently, simulated results and associated interpretations are suspect.*

We thank the reviewer for highlighting this discrepancy. We have checked our original E-AIM run and found the error that caused mass to not be conserved (input of only NO_3^- rather than NO_3^-+HNO_3). We have re-run the model with the error corrected, and have altered the text accordingly. See the specific comment regarding mass conservation in E-AIM for more details.

In addition to the above, the manuscript contains several errors; includes some points that are inconsistent with the relevant available literature; and in many instances, employs confusing, unconventional, and/or inconsistent terminology.

We apologize for any confusing terminology used. We have corrected terminology, phrasing, and inconsistencies with available literature where indicated.

Finally, many of the figures are redundant. For example, the same time series of measured HNO_3 is depicted in Figs. 1a and 6b; the same time series of measured particulate NO_3^- is depicted in Figs. 1a, 3c, and 6a; the same average diurnal cycle in measured HNO_3 is depicted in Fig. 7b, 7d, and S2; the same average diurnal cycle in measured particulate NO_3^- is depicted in Figs, 7b, 7d, and S3b, the same diurnal cycle in HNO_3 simulated with ISORROPIA is depicted in Figs. 7b, S2, and S3c; the same diurnal cycle in particulate NO_3^- simulated with ISORROPIA is depicted in Figs. 7b and S3c; and the same diurnal cycles of both HNO_3 and particulate NO_3^- simulated with E-AIM are depicted in Figs. 7d and S3d. Multiple depictions of the same information is unnecessary and not an efficient use of journal space. These figures should be consolidated.

We have removed the NO_3^- and HNO_3 time series depicted in panels a and b of Figure 6. We have also removed the ISORROPIA and E-AIM diurnal cycles depicted in figures in the supplemental (previous Figures S3c and S3d) and instead reference them in Figure 7 in the main text. We have consolidated the previous Figure S3 and S4 into one figure (now Fig S4). We have removed the repeated HNO_3 data from Figure S2 (now Figure S3). However, we would like to keep the diurnal traces of NO_3^- and HNO_3 in Figures 7b and 7d and Figure S4. In each separate figure the diurnal profiles are compared with a new dataset and we believe the repetition of these data adds clarity to the comparisons presented. We would also like to keep the NO_3^- time series in Fig 3c, as again, we believe it adds clarity in a new comparison we make in the figure.

Specific Comments

Page 13,830, lines 16-17. It would be helpful to include a citation in support of the suggestion that significant NO_x *is oxidized in the aqueous phase.*

This line has been removed, as it is not relevant to our analysis.

Page 13,830, lines 19-20. Suggest clarifying that the total aerosol concentration referred to here corresponds to non-water aerosol mass. Later, hydrated aerosol masses are presented and interpreted.

Text has been clarified.

Page 13,830, line 26 through page 13,830, line 19. This manuscript focuses on multiphase processes over the SE US during summer when relative humidities are typically high and virtually all aerosols exist as either completely deliquesced droplets or mixed phase particles that include insoluble and aqueous components. As such, it would be more appropriate to discuss the gas-aerosol phase partitioning of HNO_3 *and* NH_3 *in the context of solutions containing dissolved ions rather than individual compounds. In addition, in all airmass types,* HNO_3 *and* NH_3 *partition with all deliquesced aerosol size fractions simultaneously based on their corresponding thermodynamic properties (temperature-dependent Henry's Law,* K_h *in M / atm, and dissociation constants,* K_a *or* K_b*, respectively, in M). The same relationships apply under all conditions. There is no fundamental distinction in this regard between processes involving clean versus polluted conditions or between processes involving chemically distinct supermicron versus submicron-diameter particles.*

For example, the thermodynamic expression describing the equilibrium phase partitioning of HNO_3*,*
$HNO_{3g} -(K_h)> HNO_{3aq} -(K_a)> NO_3 + H$ *(1)*
can be reorganized and written explicitly as
$HNO_{3g} = (\{NO_3^-\} * \{H^+\}) / (K_H * K_a)$ *(2)*
where activities are in M and HNO_{3g} *in atm. Note that* NH_3, NH_4^+, H_2SO_4, *and* SO_4^{2-} *do not appear in the above expression. A similar expression can be written for the equilibrium phase partitioning of* NH_3 *based exclusively on its temperature-dependent*

thermodynamic properties, partial pressure of NH_3 in the gas phase, and solution activities of NH_4^+ and H^+, which vary as functions of aerosol liquid water content (and thus RH and temperature) and ionic strength. While HNO_3 and NH_3 (as well as other species) in the multiphase system certainly influence the phase partitioning of each other indirectly through effects on aerosol hygroscopicity, liquid water content, and acidity, phase change does not involve direct reactions between HNO_3 and NH_3 as suggested by the authors at the bottom of page 13,830 and in equation R1 of the manuscript. For example, if H_2SO_4 were added to an aerosol solution that was in equilibrium with HNO_3 and NH_3 in the gas phase, it is evident from their respective thermodynamic properties that the increased acidity would drive HNO_3 evaporation from and NH_3 condensation into the aerosol solution to reestablish new thermodynamic equilibria. These differential phase changes in response to added acidity are not entirely consistent with the discussion on page 13,831 (lines 5 to 12).

It is also unclear what is meant by the term "excess SO_4^- (lines 6-7). What is SO_4^- in excess of? Also, is "SO_4^-" supposed to be "SO_4^{2-}" or "HSO_4^-"? The text should be corrected.

I encourage the authors to revise this section of the manuscript to more accurately describe the associated thermodynamic processes and, given the focus of their analysis, to discuss these processes in the context of deliquesced aerosols containing dissolved ions.

Page 13830 line 26 though page 13831 line 7 of the text has been revised to better reflect the relevant thermodynamic processes and is now discussed in terms of dissolved ions rather than reactions of individual compounds. For example, the phrase "In highly acidic environments, typically dominated by excess SO_4^-, the semi-volatile NH_4NO_3 will dissociate (Stelson and Seinfeld, 1982)" (pg 13831 lines 5-6) has been changed to "Addition of acidic H_2SO_4 to the aerosol system, as occurs in environments dominated by SO_2 pollution, will drive NH_3 condensation into and HNO_3 evaporation from the particles as the aerosol system reestablishes a new thermodynamic equilibrium. The NH_3 driven into the particle phase will associate with sulfate, leaving HNO_3 in the gas phase (Stelson and Seinfeld, 1982)." R1 has also been changed to reflect the role of H_2SO_4 in the dissociation of NH_4NO_3. In addition, the discussion on page 13831 (lines 5 to 12) has been separated into a new paragraph.

The term "excess SO_4^-" has been clarified to mean high concentrations of sulfate, and the typographical error (SO_4^-) has been changed to SO_4^{2-}.

Page 13,832, lines 1 to 6. A large body of evidence is inconsistent with the primary points made in this section. The text should be revised to give a more balanced perspective. First, model calculations indicate that equilibration times for HNO_3 and other soluble gases with submicron- diameter aerosol size fractions are indeed on the order of minutes [e.g., Meng and Seinfeld, 1996, Atmos. Environ.]. However, equilibration times with the supermicron size fractions that dominate marine aerosol mass are typically on the order of an hour to a day or more [e.g., Erickson et al., JGR]. In addition, most particulate

NO_3^- in marine air is associated with supermicron-diameter size fractions [e.g., Huebert et al., 1996, JGR; among many others] that have much shorter atmospheric lifetimes against dry deposition than gaseous HNO_3. Consequently, and in contrast to the authors' suggestion, the uptake of HNO_3 by marine aerosol decreases (rather than increases) the atmospheric lifetime and associated transport of total NO_3 (gaseous HNO_3 plus particulate NO_3^-) relative to upwind continental regions [e.g., Kane et al., 1994, Atmos. Environ.; Stokes et al., 2000, Tellus; Russell et al., 2003, JGR; among others].

We thank the reviewer for highlighting this discrepancy. The text on page 13832 lines 1-6 has been changed to more accurately reflect the available literature on aerosol partitioning times. The equilibrium partitioning times for HNO_3 on sea salt particles has been corrected from "on the order of minutes" to "on the order of 5 to 20 hours" with updated references.

Relative to marine aerosol, influences of crustal dust on the lifetime and transport of total NO_3 differ somewhat because (1) mass median diameters for dust (~2-μm diameter [e.g., Arimoto et al., 1997, JGR]) are typically less than those for marine aerosol, and thus the corresponding mass-weighted dry-deposition velocities and fluxes of dust are also relatively lower and (2) significant amounts of dust are lofted over source regions and subsequently transported above the planetary boundary layer (PBL) where particles of similar size have longer lifetimes against deposition relative to those within the PBL where most marine aerosol resides.

Finally, the equilibrium times with particles relative to corresponding dry-deposition fluxes of gaseous HNO_3 is not the only or even the primary factor that influences variability in the atmospheric lifetime and transport of total NO_3 as a function of phase partitioning. As noted above, the dry-deposition rates of the size-resolved particles with which HNO_3 partitions must also be considered. Moderate equilibration times with relatively shorter-lived supermicron particles in marine air leads to shorter atmospheric lifetimes for total NO_3 relative to HNO_3 (see above citations). In contrast, very rapid equilibration times with longer-lived submicron particles leads to longer atmospheric lifetimes for total NH_3 (gaseous NH_3 plus particulate NH_4^+) relative to NH_3 [e.g., Smith et al., 2007, JGR].

Again, we thank the reviewer for pointing out these discrepancies between the literature and the discussion on page 13832. The relevant text has been updated to give a more nuanced view of total NO_3^- lifetime and transport as a result of HNO_3 uptake on sea salt and dust aerosol. Revisions include indicating that marine aerosol tends to decrease atmospheric lifetime and transport of total NO_3^-, while the effect of mineral dust on NO_3^- differs due to size and lofting differences relative to marine aerosol.

Section 2.2 starting on page 13,833. The inlets for the MARGA and the SMPS/APS are described in detail but those for the other sampling systems are not. The inlet design and elevation for each system should be reported. Was air sampled at the same height by all instruments? If quantified, passing efficiencies of analytes through the inlets should also be reported. The measurement location (height and distance) for meteorological *conditions used in the model calculations relative to the chemical measurements should also be specified.*

The MOUDI was sampled using a PM_{10} cyclone, at an elevation of 1 m above ground level. The XRF measurements were collected using an inlet 5 m above ground level with a flow rate of 1.25 L/min, followed by two annular denuders in series (sodium bicarbonate and citric acid) and collected with a 47-mm diameter, 2-μm nominal pore size-ringed Teflon filter. The meteorological measurements were located approximately 10 m from the MARGA instrument, and were taken about 9 m above ground level. The MOUDI is a well-established impaction based technique that does not have known efficiency issues for particles of specific compositions, but specific transmission characterization was not conducted for this study. There are known issues with respect to which stage particles are detected on in dry environments related to bounce, but due to the high water content at the Centreville site we do not expect any significant impacts from particle bounce. To our knowledge, passing efficiencies of specific analytes for SMPS/APS were not assessed. These details for specific instrumentation have been added to the relevant subsections in Section 2.2 of the text.

Page 13,833, lines 17-18. Detection limits for field measurements of gases and aerosols typically vary over space and time as functions of (1) air-mass types and meteorological conditions, (2) instrumental conditions (including the age and history of chromatographic columns), (3) deployment configurations (including the length, diameter, material, and surface preparation of inlets), and (4) the skill and experience of operators (calibration, data reduction, etc.). Method detection limits estimated by a different research group working with a different instrument deployed at a different location under different environmental and operating conditions almost certainly varied significantly from those for the MARGA deployed during SOAS. The authors should estimate and report MDLs for their measurements based on available quality-assurance evaluations performed during the campaign. By what method and how frequently was the instrument calibrated, how was performance during SOAS evaluated, and how was data quality assured?

The MARGA system is designed for robust, long-term monitoring applications, and thus continuously performs many automated quality control self-checks. For example, the MARGA monitors all internal pressures and flows, as well as ambient and shelter temperatures and relative humidities to take into account system diagnostics. To check the quality of reported data, the MARGA uses a Li^+ (320 ug/L) and Br^- (3680 ug/L) internal standard with which all data is compared. The MARGA thus performs a continuous calibration, and monitors the chromatographic column for potential degradation. The instrument makes automatic adjustment for the age and history of the chromatographic column, such as adjusting the temperature-controlled oven around each column to ensure chromatographic peaks remain separated. Notes to this effect have been added to the MARGA description in the text. Unfortunately we do not have MDLs from our specific instrumental setup. However, given the similarities between the manufacturer's reported MDLs and those independently reported by Makkonen et al. (2012) and Rumsey et al. (2014), we believe the MDLs from our system to be very similar.

Page 13,834, lines 21 to 22. How frequently were the MOUDI samples recovered for single- particle analysis? Later in the manuscript (page 13,844), the authors report data for 12 samples collected during the first event on (9 to 13 June) but only 3 samples collected during the second (23-28 June). Why the big difference in sample numbers for events of similar length?

For most of the field campaign, MOUDI samples were collected every 11 hours (8am-7pm and 8pm-7am) yielding a daytime and nighttime sample. On certain days of the field campaign, during "intensive" periods, which were time periods predicted to be of particular interest, samples were collected every 3 hours during the day to give better time resolution (8am-11am, 12pm-3pm, 4pm-7pm, 8pm-7am). During period one (June 9-13) and period two (June 23-28) discussed in the paper, June 10-12 were "intensive" periods. Thus, instead of only one daytime collected for each of these three days, 3 daytime samples were collected, leading to a greater number of samples analyzed. Additionally during period two, MOUDI samples were not analyzed for all of the days of the study since some of the TEM grids were damaged in the field and unusable.

The sampling frequency has been added to Section 2.2.2 of the text to clarify this point for readers.

Page 13,838, lines 14-15. The reported units for gas phase mixing ratios are inconsistent with those for corresponding mass concentrations. Assuming that the mass units are correct, "ppm" should be changed to "ppb"

Thank you for pointing out this typographical error; units have been changed to ppb.

Page 13,838, lines 15-18. Presumably, the photochemical production of HNO_3 from NO_x during daytime coupled with the enhanced photochemical production and condensation of other soluble acids during daytime (e.g., H_2SO_4 from SO_2 oxidation), associated aerosol acidification, and resulting shift in HNO_3 partitioning towards the gas phase would have also contributed to the observed day-night variability.

Consideration of day/night variability of HNO_3 from photochemical production of HNO_3 from NO_x and acidity changes from photochemical H_2SO_4 production and condensation has been added to the text following page 13838, line 18.

Page 13,838, lines 20 to 25, and Supplement. The large differences in average HNO_3 concentrations measured over diurnal cycles with the MARGA and co-located ARA and CIMS instruments as well as the large differences in average particulate NO_3^- measured over diurnal cycles with the MARGA and the ARA (Fig. S3a) strongly suggest that some of these data are significantly biased. At night, mean HNO_3 concentrations measured with the MARGA were higher than those measured with the ARA by about 50% to 75% whereas, during midday, mean concentrations measured with the MARGA were lower by about 50%. Similar differences in absolute and relative variability in mean HNO_3

concentrations measured by these two instruments were evident during both "dust" and "non-dust" periods (Fig. S4). During all periods, mean HNO_3 *concentrations measured with the MARGA where higher than those measured with the CIMS by about 10% to 70%, with the greater divergence evident at night (Fig. S3a). The authors speculate that diurnal variability in the direction and magnitude of bias between the MARGA and ARA results reflect damping of diurnal variability via wall effects within the long MARGA inlet. They also speculate that the higher elevation of the CIMS' inlet may explain systematic divergence between* HNO_3 *concentrations measured by MARGA versus CIMS.*

The mean particulate NO_3^- *concentrations measured with MARGA were systematically higher than those measured by ARA by factors of 2 to 4 and diurnal variability also differed systematically (Fig. S3b). In addition, mean* NO_3^- *concentrations measured by the two instruments diverged to a much greater degree during "dust" relative to "non-dust" periods (Fig. S4). The authors present evidence supporting the hypothesis that these difference were driven in part by the inefficient removal of particles larger than 2.5-μm diameter by the cyclone on the MARGA inlet. However, it is unclear how such an effect would cause diurnal cycles in mean concentrations to diverge. The authors also speculate that the ARA measurements of particulate* NO_3^- *may be biased low by less than 10% but, if so, this effect would account for only very minor fractions of the large differences evident in reported data for the two instruments.*

I encourage the authors to also compared their data with paired data for HNO_3 *and particulate* NO_3^- *measured as part of EPA's routine monitoring program at the site (see web site cited on page 13,832, line 24). Although EPA's filter samples integrated over longer periods, they would still provided useful additional benchmarks against which to evaluate the reliability of data generated by the MARGA.*

Based on available information presented in the manuscript, it is entirely unclear if the authors are interpreting aspects of real or artifact behavior in HNO_3 *and particulate* NO_3^- *measured with the MARGA.*

The reviewer raises a fair point about the reliability of the HNO_3 and NO_3^- data, particularly given the differences in the measurements of these species between different instruments. In regards to the differences in NO_3^-, we believe the main difference between the instruments is due to the different efficiencies of the $PM_{2.5}$ size cut. As indicated in Fig S7, the aerosol mass distribution peaked between 2 and 3 $\mu g\ m^{-3}$ and the majority of NO_3^- at the SOAS site appears to be associated with aerosol near this size fraction. Thus, small differences in sampling efficiency may have large effects on the amount of NO_3^- sampled.

We thank the reviewer for the suggestion to compare HNO_3 and NO_3^- measurements with those taken by the routine monitoring station at the site (see website cited on page 13832, line 24). This routine monitoring is conducted by ARA, so this specific comparison was already done in the paper. However, in order to better understand the NO_3^- measurement discrepancies we have added comparison to measurements with two additional instruments: the EPA's filter pack and an AMS operated by a group from the University of Colorado, Boulder. These additional datasets have been added as Figure S5 and corresponding discussion has been added to the supplemental text. Briefly, we find that the EPA, which was located approximately 100 km north of the sampling site and also employed a $PM_{2.5}$ size cut, measured NO_3^- higher than ARA but lower than MARGA. In addition, the EPA measurements also indicate high NO_3^- during the second coarse particle event as found by MARGA (data from the EPA is not available during the first coarse particle event), suggesting that this event was regional in scope. In addition, we compare dataset with NO_3^- measured by an AMS, which sampled with a PM_1 size cut. We note that the ARA NO_3^- reported concentrations are very similar to those reported by the AMS. Together these data suggest that the MARGA may have a size cutoff above the nominal $PM_{2.5}$ size cut while ARA may have a cutoff below 2.5 μm. The difference in diurnal cycles between the MARGA and ARA may thus be partially due to the difference in sampled NO_3^- (i.e. MARGA samples more supermicron NO_3^- while ARA samples fine mode NO_3^- more efficiently).

Unfortunately, we have no additional datasets for further comparison of HNO_3 measurements beyond those of MARGA, ARA, and the Caltech CIMS. We continue to believe that wall effects within the MARGA inlet may be a reason for discrepancies in HNO_3 measurements, in addition to the higher elevation of the CIMS instrument. However, given the similarity between the MARGA and CIMS average diurnal cycle (Figure S4) for HNO_3 and the reasons stated above for NO_3^-, we believe we are interpreting real behavior in HNO_3 and aerosol NO_3^- and that these measurements are useful to the atmospheric chemistry community.

Page 13,839, lines 7 to 13, and Fig. 2 caption. Ions (e.g., NH_4^+*) do not "neutralize" ions (e.g.,* SO_4^{2-}*). Dissolved* NH_3 *neutralizes* H^+ *contributed by all acids. The text should be corrected.*

Text has been corrected from "insufficient to fully neutralize existing sulfate" to "insufficient to fully balance existing sulfate" in both the main body and in the Fig 2 caption.

Page 13,839, lines 16 to 21. H^+ *concentrations inferred from ion imbalances based on measured ionic constituents are associated with relatively high accumulated analytical uncertainties. Certainly at the lower end (and possibly over much) of the inferred range,* H^+ *concentrations are less that the corresponding detection limits based on accumulated uncertainties and should be reported as such.*

Based on the minimum detection limits given by Makkonen et al (2012), the accumulated uncertainty in the H^+ concentration is 6 nmol m^{-3}. This uncertainty has been added to the reported H^+ concentration in the text.

In addition, these results are based on $PM_{2.5}$ *(or larger) sampled in bulk and, consequently, measured concentrations of analytes correspond to a mixture of chemically distinct size fractions. It is highly unlikely that* H^+ *inferred from the composition of bulk* $PM_{2.5}$ *is representative of all corresponding size fractions in ambient air. This important* *point should be mentioned.*

We do not mean to suggest that the inferred H^+ from bulk $PM_{2.5}$ is representative of all size fractions and this point has been added to the relevant section of the text.

Finally, acids for which anions were not measured (primarily organic species such as $(COOH)_2$*) also contribute non-trivial amounts of acidity in aerosol solutions. It is evident from equation 1 that ignoring such unmeasured anions would introduce positive bias in the inferred* H^+ *concentrations. Consequently, these estimates should be reported as lower limits for bulk* $PM_{2.5}$ *[e.g., see Hennigan et al., 2015, ACP].*

We agree with this point that the inferred H^+ is likely a lower estimate of acidity due to the presence of other acids (organics, e.g.) that are not included in the calculation. This point has been added to the text.

In general, we do not mean to suggest that the reported H^+ should be taken as an absolute measure of aerosol pH at the SOAS ground site. Instead, the H^+ concentration inferred by ion balance is used to support the idea that the aerosol at SOAS was acidic, which provides the basis for further chemical analysis in the text. The readers are pointed to Guo et al 2014, who provide a much more thorough and quantitative analysis of aerosol pH during the campaign.

Page 13,840, line 6. Based on standard usage, the term "total acidity" (not "strong acidity") typically used to describe the combined contributions of H from ionized and undissociated acids. "Strong acidity" typically refers to H^+ *contributed by acids that are essentially completely dissociated at a given ionic strength, "weak acidity" typically refers to* H^+ *contributed by acids that are partially dissociated at a given ionic strength, and typically refers to total H (ionized + undissociated) contributed by all acids at any ionic strength. In other words, assuming no phase changes, total acidity in solution is conservative with respect to ionic strength whereas strong and weak acidities are not.*

We thank the reviewer for indicating this error on our part; the text has been revised accordingly from "strong acidity" to "total acidity."

Page 13,840, lines 13 to 20. Again, the terminology here is confusing. HNO_3 *and* NH_3 *partition with all aerosol size fractions as a function of solution acidity. Particulate* NH_4^+ *is not associated preferentially with* SO_4^{2-} *or* NO_3^-*. Based on their thermodynamic properties,* NH_3 *partitions preferentially with the more acidic submicron size fractions because its solubility increases with increasing acidity. Conversely,* HNO_3 *partitions preferentially with the less acidic supermicron size fractions because its solubility increases with decreasing acidity.*

This section of the text has been rephrased to clarify that the partitioning of nitrate and ammonia is due to the changes in acidy, caused by the changes in ion species, rather than by the presence of the chemical species themselves. For example, the phrase "The formation of fine mode aerosol NO_3^- is limited by the availability of any NH_4^+ not already associated with sulfate" has been changed to "The formation of fine mode aerosol NO_3^- is therefore limited, as only the NH_4^+ not already associated with sulfate will be free for the potential formation of NH_4NO_3."

Page 13.840, line 23. No aerosol size or mass data are reported for "coarse particle event 2" so what is the basis for referring to it as such? If size is assumed based on composition as appears to be the case, this should be explained or, preferably, the events should characterized based on measured composition (e.g., "high NO_3^- *event" rather than the assumed size.*

The size distribution of $PM_{2.5}$ during the second event was assumed to be similar to that of the first coarse particle event 1 due to similarities in aerosol composition. A note to this effect as been added to the text.

Page 13,840, lines 24 to 27, top of next page, and elsewhere in the manuscript. It is unclear why the authors characterize these base cations as "mineral species". Certainly, these species may be associated with mineral aerosol produced from deflation of surface soils but they are also components of primary marine aerosol produced at the ocean surface, particles produced from biomass burning, and fly ash from fossil-fuel combustion. Since the authors suggest later that contributions from both marine and crustal aerosol are important, to minimize the potential for confusion, I encourage them to refer to these constituents as "base cations" rather than "mineral species."

We thank the reviewer for pointing out the potential confusion regarding usage of the term "mineral species." We feel that the term "base cations" may also create confusion because "base cations" can also refer to NH_4^+ or positively charged organics (e.g. amines). We have decided to use the term "mineral species" to include cations from both sea spray, crustal dust, and other sources such as biomass burning, fly ash, etc. We have altered the text to use the term "crustal dust" to indicate when we are speaking only of cations from dust sources.

In addition, as indicated above, NO_3^- *concentrations are "primarily drive" by solution acidity not "by availability of these cations." Again, ions do not "neutralize" ions. Finally, it is evident from equation 2 above (and from the thermodynamic models used by the authors to interpret their data) that* HNO_3 *is infinitely soluble in neutral or alkaline solutions (as* H^+ *goes to 0.0,* HNO_{3g} *goes to 0.0) so, if all acidity were neutralized as suggested here, gas-phase mixing ratios of* HNO_3 *would also be zero, which is inconsistent with the authors' measurements.*

The text has been revised to include these corrections. The phrase "These two events correspond with an increase in mineral species…suggesting NO_3^- is primarily driven by the availability of these cations and resides in the coarse mode" has been changed to "…suggesting that during these periods, the mineral cations decreased aerosol acidity enough to drive HNO_3 into the aerosol phase as coarse mode NO_3^-." We do not mean to suggest that the aerosol at SOAS was neutral or alkaline; both our own measurements and those by Guo et al suggest the aerosol was always acidic. Instead, we meant to suggest that enough mineral cations were present to balance (via charge equivalents) the measured NO_3^-, although we note that there was not enough to balance both NO_3^- and free SO_4^{2-} (hence the aerosol was still acidic). The text has been clarified on this point.

Fig. 3. Since the masses depicted in panel a correspond to hydrated aerosols, most of the mass is contributed by water and some of the variability in mass is driven by variability in RH rather than associated ionic species. I suggest that another panel be added to the figure depicting RH and temperature over the period of record to provide context for evaluating variability in the data for hydrated mass depicted in panel a. The caption should also indicate that the masses in panel a correspond to those of hydrated aerosols.

The caption of Fig 3 panel a has been clarified to indicate that the masses in panel a of the figure correspond to hydrated aerosol. We thank the reviewer for the suggestion of adding another panel to Fig 3 to depict temperature and relative humidity. However, we feel the panel does not substantially add any information to the figure (there is no obvious correlation between RH or temperature and aerosol mass) and so we have placed the time series of RH and temperature in the supplemental information and reference it in the main text.

Page 13,841, lines 1 to 11 and Fig. 3 caption. I am confused by the reported interpretation of these results. If, as suggested by the authors, the particles that contained NO_3^- were "fully neutralized," HCl would not be displaced by HNO_3. HCl displacement is driven by acidity. Based on its thermodynamic properties, neutral aerosols are a sink not a source for gaseous HCl. However, relative to corresponding ratios in seawater and in crustal dust, the low concentrations of Cl^- versus Na^+ during the first event and the complete absence of Cl^- during the second suggest that these aerosols were highly acidic. How do the authors account for these unusual seemingly inconsistent relationships?

Again, we did not mean to suggest that overall the aerosol at SOAS was neutral or basic. Enough cations were present to charge balance NO_3^-, but not to charge balance the sum of inorganic anions and hence the aerosol was acidic. Thus the low concentrations of Cl^- are consistent with interpreted relationships. As mentioned in the above, the text has been revised to remove suggestion that aerosol was not acidic.

The caption for Fig. 3 seems to refer only to the first event. For example, the caption indicates that "periods of high aerosol NO_3^- during the SOAS campaign were correlated with high PM_1- PM_2 aerosol mass fraction" and "high Na^+ and Cl^- concentrations". However, mass data are reported for only the first high NO_3^- event and virtually no Cl^- was measured during the second. The text should be revised accordingly.

We thank the reviewer for highlighting this discrepancy. The caption of Fig. 3 has been revised to indicate that high PM_1-$PM_{2.5}$ mass fraction and Cl^- were observed only for the first coarse particle event. The main body text corresponding with these observations has also been altered to indicate that high Cl^- occurred only during the first high NO_3^- event.

Because both marine aerosol and crustal dust contain supermicron Cl^- and Na^+, the *rationale for attributing the reported* Cl^- *and* Na^+ *during these periods to marine aerosol (Fig. 3 caption) is unclear. In the second paragraph on page 13,841(lines l2 to 19), the authors indicate that mineral aerosol also contributed to the higher aerosol mass concentrations during this period. In addition, elsewhere in the manuscript (e.g., caption for Fig. S4), these periods are referred to as "dust events" with no mention of sea salt. Which is it, marine aerosol, crustal aerosol, or some combination of the two? The text and the captions should be revised for consistency.*

The first event was likely a combination of both sea spray and crustal dust. In Section 3.3, for example, we suggest that both sea spray and crustal dust were present during both events, but that the first event was more strongly influenced by sea spray than the second event. We have revised the text in Section 3.2, Fig. 3, and Fig. S4 to indicate that the coarse particles were likely a combination of sea spray and crustal dust.

The legend refers to nss Na^+ *whereas the caption refers to* $Na^+_{residual}$*. Are these supposed to be the same quantities? If not, what is nss Na+ and how was it calculated?*

The term "nss Na^+" was a typographical error on our part and has been corrected to "$Na^+_{residual}$."

What is the rationale for inferring that the trends in Na^+ *and* Ca^{2+} *during the first event "support the conclusion that* NO_3^- *is predominately formed by displacement reactions of NaCl,* $CaCO_3$*, and other similar species?" Other than their influence on activity coefficients,* Na^+ *and* Ca^{2+} *are chemically inert with respect to the thermodynamic processes under consideration here. Consequently, in and of themselves, trends in these species provide no relevant information regarding "displacement reactions." In addition, the term "displacement reactions" involving* HNO_3 *and marine aerosol is normally used to refer to the acid displacement of HCl not NaCl.* Na^+ *is not displaced. Also, reaction of* HNO_3 *with* $CaCO_3$ *involves titration not displacement.*

The rationale behind using trends (as indicated in Fig 3) to infer that aerosol NO_3^- is formed by reaction with NaCl and $CaCO_3$ is due to the close correlation between observed NO_3^- and observed mineral species. Although this might not directly indicate a relationship between the two, the presence of the mineral species appears to allow greater concentrations of NO_3^- aerosol to occur, likely due to the minerals providing a reactive surface if not by a thermodynamic process. The text has been modified to explain this reasoning. In addition, the term "displacement reaction" has been removed.

Similarly, Ca^{2+} *is not displaced. Finally, to what "other similar species" are the authors referring?*

The phrase "displacement reactions of NaCl, $CaCO_3$, and other similar species" has been replaced with "reactions involving sea spray and crustal dust."

Virtually all measurements of size-resolved marine aerosol and crustal aerosol reveal non-trival concentrations of nss SO_4^{2-} *and* NH_4^+ *associated with supermicron-diameter* *size fractions and non-trivial concentrations of NO_3^-, Cl^-, and Na^+ (and other chemically conservative cations) associated with submicron-diameter size fractions. The authors' analysis seems to be based on the implicit but unstated assumption that all nss SO_4^{2-} and NH_4^+ measured in samples of bulk $PM_{2.5}$ is submicron and all NO_3^-, Cl^- and Na^+ (and other conservative cations) is supermicron, which is almost certainly not the case. This assumption should be stated and the associated implications for data interpretation discussed. It is impossible to reliably evaluate thermodynamics of the phase partitioning of gases with chemically distinct aerosol size fractions based on the chemical composition of $PM_{2.5}$ sampled in bulk.*

Although we do believe the majority of sampled SO_4^{2-} and NH_4^+ to be in the submicron-diameter size fraction, we do not mean to imply that *all* SO_4^{2-} and NH_4^+ is submicron. We agree with the reviewer that there is likely some SO_4^{2-} and NH_4^+ in the supermicron size fraction and some NO_3^-, Cl^-, and Na^+ and other mineral cations in the submicron size fraction.

We acknowledge that the lack of distinct aerosol size fraction data is one of the limitations of our analysis. However, we do present CCSEM-EDX, which provides some size-resolved, chemically distinct composition data. As seen in Fig. 5, for example, we note that there is some sea spray and crustal dust aerosol in the submicron region. In addition, comparison with the AMS that employed a PM_1 size cut shows that the aerosol at the SOAS site did contain submicron NO_3^-. Figure S6 (in the revised supplemental) indicates that the MARGA ($PM_{2.5}$) measured significantly higher NO_3^- concentrations than the AMS (PM_1) during times of high aerosol surface area (which also occurred at times of higher concentrations of mineral species and higher PM_1-$PM_{2.5}$ aerosol size fraction). We believe observation substantiates our claim that mineral species allowed supermicron NO_3^- to form episodically during the SOAS campaign.

Page 13,841, lines 21-23. On page 13,835, the authors describe explicit fingerprinting approaches that were used to identify the likely sources of individual particles sampled in parallel with MARGA yet they open this paragraph by discussing sources based on rather vague relationships involving "the prominence of both Ca^{2+} and Na^+". Why were sources not evaluated based on the fingerprinting approach described previously? Later in the paragraph and on the following page, they infer sources based on comparison of ratios for conservative species in samples relative to those in seawater

The fingerprinting technique described on page 13835 (CCSEM-EDX) was used to identify sea spray and crustal dust particles. Some results from this technique have been moved to Section 3.3 to discuss the differences in composition between the two mineral dust periods, although the majority of discussion of the CCSEM-EDX results is in in Section 3.4 (and accompanying Fig. 5). The ratios used in Section 3.3 (page 13841 – 13843) were evaluated using MARGA and XRF data. The first sentence of the paragraph has been changed to reflect that MARGA and XRF were used to evaluate mineral species origin.

Page 13,841, lines 23-25. The rationale for differentiating aerosol sources based on *relative concentrations of* Cl^- *is unclear. First, particulate* Cl^- *is not chemically conservative with respect to source and second, at least some mineral aerosol contains* Na^+ *and* Cl^- *in concentration ratios similar to those in seawater [e.g., Young et al., 2013, JGR; Jordon et al., 2-15, JGR].*

We acknowledge that some mineral aerosol contains Na^+ and Cl^- in concentration ratios similar to those in sea spray, and have added the suggested references to the text. However, based on elemental ratios of Cl^-, Na^+, Ca^{2+}, and the CCSEM-EDX results, we continue to believe that the first event was more strongly (although not entirely) influenced by sea spray than the second event. From the CCSEM, the individual particle ratios of Na to Mg were the same ratio as seawater in the class of particles identified as such in Figure 5.

Page 13,842, lines 7 to 9. Like HNO_3*, the phase partitioning of HCl with* $PM_{2.5}$ *is based primarily on thermodynamics not directional, time-dependent kinetics. Consequently, the rationale for interpreting* Cl^- *depletion in terms of "longer air mass transport" time is unclear.*

We do not mean to suggest that the phase portioning of HCl with $PM_{2.5}$ is based on directional, time-dependent kinetics. Rather, we suggest that because the reaction of HNO_3 on sea spray takes many hours to a day to equilibrate, the longer air mass transport would have provided sufficient time for Cl^- to partition to HCl. The timescale of air transport from the coast to the SOAS site is comparable to the equilibrium partitioning time (see Figure 4), particularly during the first event. Therefore the air mass that traveled slower would have less Cl^- present than a faster air mass. This point has been clarified in the text.

Page 13,844, lines 1 to 6. The authors should explain why the number of samples (12) reported for the first event on 9-13 June is substantially greater than that (3) reported for the second event on 23-28 June. Was each MOUDI deployed for longer periods during the second event or was part of the second event not sampled and characterized for single-particle composition? If the latter, what are the implications for data interpretation?

A response to a similar comment regarding the number of MOUDI samples for period 1 and period 2 is given above. Some of the implications for data interpretation since MOUDI samples from fewer days during period two were analyzed include that because a lesser number of particles were analyzed for period two, there is likely greater error associated with calculations. This point has been added to the relevant section in the text.

Although the percentages of mineral particles during the event versus non-event periods differ to relatively greater degrees (27% and 53% during periods 1 and 2, respectively, versus 17% during other periods), those for marine aerosol are more similar (20% and 23% during periods 1 and 2, respectively, versus 16% during other periods). Given the variabilities among percentages for individual samples comprising each group, are these latter differences significant and, if not, what are the implication for the reported *interpretations? For example, if statistically indistinguishable amounts of marine aerosol were present during all periods, then reactions involving sea salt are not the primary explanation for the moderately higher NO_3^- concentrations during the events. Are the sizes of the dust and marine aerosol particles larger during event versus non-event periods?*

Using the p-test at the 95% confidence interval, the variabilities among percent of marine aerosol during the first period, second period, and other remaining periods are all statistically significant. The sizes of dust and marine aerosol particles during event versus non-event periods are comparable.

Page 13,844, lines 12 to 13. Is it reasonable to assume that minimal amounts of N were lost from aerosol samples in a vacuum? This assumption should be justified based on available evidence.

Yes, it is reasonable to assume that minimal amounts of N were lost in the vacuum since nitrogen was most frequently found in the fairly nonvolatile form of $NaNO_3$. See references below for SEM-EDX analysis of nitrate particles (primarily $NaNO_3$) under vacuum showing a lack of volatility.[1,2] This justification and relevant references has been added to the text.

1. Laskin, A.; Iedema, M. J.; Cowin, J. P., Quantitative time-resolved monitoring of nitrate formation in sea salt particles using a CCSEM/EDX single particle analysis. *Environmental Science & Technology* **2002,** *36*, (23), 4948-4955.
2. Laskin, A.; Iedema, M. J.; Ichkovich, A.; Graber, E. R.; Taraniuk, I.; Rudich, Y., Direct observation of completely processed calcium carbonate dust particles. *Faraday Discussions* **2005,** *130*, 453-468.

Section 3.5 starting on page 13,844. Earlier, the authors argue that the gas-aerosol equilibration times for HNO_3 with $PM_{2.5}$ aerosol is less than 30 minutes. Given the average atmospheric lifetimes of particles in this size range (many days to couple weeks), it appears that solubility rather than surface area is the primary control on HNO_3 uptake. If so, what is the relevance of this section for the overall analysis?

We have corrected our argument to indicate that gas-aerosol equilibrium times for HNO_3 with $PM_{2.5}$ aerosol are more likely on the time scale of hours to a day, rather than less than 30 minutes. Given consideration of this new timescale and the strong correlation between high NO_3^- and aerosol surface area, we believe that surface-area is still the primary control on HNO_3 uptake.

Fig. 7 caption. It appears that panels a and c depict individual hourly measurements of HNO_3 by MARGA and panels b and d depict diurnal profiles of HNO_3 and particulate NO_3^- measured by MARGA, presumably binned by hour and averaged over the entire duration of the campaign. The nature of the measurements depicted in the panels and the corresponding periods of record should be clarified in the caption.

The caption for Fig. 7 has been clarified on these points.

Section 3.6, starting on page 13,846, line 5, and Fig. 7. Something is wrong here. To my knowledge, both ISORROPIA and E-AIM conserve mass. Assuming that both models were initialized with identical chemical data, the simulated partitioning of HNO_3 *and particulate* NO_3^- *may vary differentially over time in response to differences in the ISORROPIA versus E-AIM schemes but the corresponding sums of simulated* $HNO_3 + NO_3^-$ *(on a molar basis) should be conserved and exhibit the same temporal variability in both simulations. The reported results indicate that mass is apparently conserved in ISORROPIA (i.e., the sums of measure* $HNO_3 + NO_3^-$ *at each point in time equal the corresponding sums of simulated* $HNO_3 + NO_3^-$*). However, mass was lost in E-AIM (i.e., the sums of measured* $HNO_3 + NO_3^-$ *are always substantially greater than the corresponding sums of simulated* $HNO_3 + NO_3^-$*). How do the authors account for the loss of significant total* NO_3 *(*HNO_3 *+ particulate* NO_3^-*) in E-AIM?*

We thank the reviewer for pointing out this discrepancy. Upon reviewing how the E-AIM model was implemented, we discovered that nitrate had been added into the model as only NO_3^-, rather than the sum of NO_3^-+HNO_3. We have corrected this error and rerun the model. The results of the new model run, which now shows mass conservation, are presented in Fig 7 and the text of the corresponding section (Section 3.6) has been corrected in light of these new results.

Page 13,848, line 11. It is highly unlikely that particulate NH_4^+ *would ever be present at sufficient concentrations to "balance" all nss* SO_4^{2-} *in the SE US because, based on its thermodynamic properties, the solubility of* NH_3 *in aerosol solutions decreases with decreasing acidity, which accounts for the shift in partitioning of* NH_3 *towards the gas phase with increasing aerosol solution pH. The solubility of* NH_3 *in neutral or alkaline solution is quite low.*

We thank the reviewer for this clarification. The text on page 13848, line 11 has been modified to indicate that little NH_4^+ is present, despite the high solubility of NH_3 in acidic solutions.

Supplement, page 2, section 2, par 1, and Fig S2. I don't understand the rational for interpreting diurnal variability in HNO3 based on the temperature dependence of its phase partitioning. It is evident from the diurnal variabilities in average concentrations of both HNO_3 *and particulate* NO_3^- *(Fig. 7 b and d) as well as the diurnal variability during individual days (e.g., see Fig. 1c in particular) that, on average, both* HNO_3 *and particulate* NO_3^- *increase during daytime and decrease over night. If, as suggested by the authors, the temperature dependence of phase partitioning were the primary driver of* HNO_3 *variability,* HNO_3 *would increase and particulate* NO_3^- *would decrease by approximately equal amounts on a molar basis during daytime and the opposite pattern would occur at night. The text should be clarified.*

We apologize for this confusion. We were not trying to suggest that the diurnal variability of measured HNO_3 should be solely based on the temperature dependence of its phase partitioning. Rather, we wanted to ask whether the model has the volatility right, given the discrepancies between measured and modeled diurnal profiles of HNO_3 and NO_3^-. We agree that that if the temperature dependence of phase partitioning were the primary factor, it would follow the pattern described by the reviewer. We note that we do not see this pattern manifested by either the MARGA or the ISORROPIA diurnal profiles. However, we also note that the E-AIM diurnal profile does seem to exhibit this behavior, suggesting that this model (which includes all mineral species as Na^+ equivalent rather than as individual species like ISORROPIA) might place too much reliance upon temperature-driven phase partitioning rather than other factors that might influence this partitioning.