Review of

Influence of mineral dust and sea spray supermicron particle concentrations and acidity on inorganic NO_3^- aerosol during the 2013 Southern Oxidant and Aerosol Study

by H. M. Allen et al.

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 speculations suggest that these data are significantly biased by large amounts and, thus, the utility of their interpretation is problematic.

- The aerosol data correspond to nominal PM2.5 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 PM2.5 may have little if any direct relevance to the corresponding processes in ambient air.

- 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.

- 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.

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.

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.

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.

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.

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,

$$HNO_{3g} \overset{K_H}{\leftrightarrow} HNO_{3aq} \overset{K_a}{\leftrightarrow} NO_3^- + H^+ \tag{1}$$

can be reorganized and written explicitly as

$$HNO_{3g} = (\{NO_3^-\} * \{H^+\}) / (K_H * K_a) \tag{2}$$

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 the authors mean 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 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].

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].

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.

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?

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?

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”.

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.

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.

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.

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.

In addition, these results are based on PM2.5 (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 PM2.5 is representative of all corresponding size fractions in ambient air. This important point should be mentioned.

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 PM2.5 [e.g., see Hennigan et al., 2015, ACP].

Page 13,840, line 6. Based on standard usage, the term “total acidity” (not “strong acidity) is 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 “total acidity” 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.

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.

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.

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.”

In addition, as indicated above, NO_3^- concentrations are “primarily driven” 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.

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.

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?

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 PM1-PM2 aerosol mass faction" 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.

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 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?

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.

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

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 PM2.5 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 PM2.5 sampled in bulk.

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

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].

Page 13,842, lines 7 to 9. Like HNO_3, the phase partitioning of HCl with PM2.5 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.

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?

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?

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.

Section 3.5 starting on page 13,844. Earlier, the authors argue that the gas-aerosol equilibration times for HNO_3 with PM2.5 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?

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.

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?

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.

Supplement, page 2, Section 2, par. 1, and Fig. S2. I don’t understand the rational for interpreting diurnal variability in HNO_3 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.