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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Particle water and pH in the Eastern Mediterranean: sources variability and implications for nutrients availability" *by* P. Nikolaou et al.

Anonymous Referee #3

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General Comments

This manuscript reports an analysis of the liquid water content (LWC) and acidity of submicron aerosol sampled in the eastern Mediterranean region during late summer and autumn 2012. Results are interpreted in the context of source region and associated implications for nutrient availability and primary productivity in the eastern Mediterranean region. The topic is relevant for publication in ACP, the investigation utilized state-of-the-science instruments and thermodynamic-model calculations, and results are interesting. Unfortunately, as summarized below, the manuscript suffers from several important shortcomings.

During most sampling periods, the authors did not generate the gas-phase data required to reliably estimate aerosol-solution pH using the ISORROPIA-II thermodynamic model run in the "forward" mode. In addition, as described in more detail below, the authors' estimate of 1 pH unit as a reasonable upper limit for the associated bias is unconvincing. The actual upper limit is almost certainly greater than 1 pH unit and, based on results from other coastal locations [e.g., Smith et al., 2007, JGR], the magnitude of bias would be expected to vary significantly as a function of air mass history and time of day. Consequently, it is impossible to differentiate variability in pH associated with the magnitude of bias versus variability driven by environmental factors. Because the calculated pHs for most periods are not representative of those for ambient aerosol and the associated uncertainties are largely unconstrained, these calculated values cannot be reliably interpreted and should not be reported. The LWC results are interesting and, after revision to address other issues raised herein, may be suitable for publication as the focus of a dedicated analysis.

Some of the measurement techniques and associated approaches for interpreting results are not described in the methods section and virtually no information on data quality (detection limits, precision, absolute accuracy) is reported. All methods should be described and information on corresponding data quality should be added.

The analysis is based primarily on the bulk, ionic composition of particles less than 1-μm diameter. However, as noted by the authors, mineral aerosol mass and associated liquid water is typically dominated by supermicron diameter size fractions [also see Arimoto et al., 1997, JGR; E. Reid et al., 2003, JGR]. For particles less than 1-μm diameter, dust concentrations decrease with decreasing size [e.g., Reid et al., 2003] whereas aerosol solution acidity typically increases with decreasing size [e.g., Keene et al., 2004]. Consequently, acidities based on the bulk composition of submicron aerosol may not be directly relevant to the acidities for the upper end of the submicron size distribution in which most of the submicron dust resides. In addition, the acidities of submicron aerosol size fractions are typically much greater than those of the supermicron size fractions with which most of the mineral aerosol mass is associated. It is evident that, even if the pH estimates were reliable, they would not be directly relevant to pH-dependent processes including nutrient availability involving most of the mineral aerosol, which is a major focus of the analysis.

Finally, the pH of PM10 aerosol sampled in bulk is not conservative. Sampling chemically distinct size fractions of PM10 in bulk typically drives significant artifact phase changes of compounds with pH-dependent solubilities because the pH of the bulk mixture is different than that of the size fractions with which these compounds partition preferentially in ambient air. Consequently, aspects of the manuscript involving interpretation of acidity based on PM10 composition are inherently problematic.

Specific Comments

Abstract, line 1. It is unclear what is meant by "drives the aerosol phase." Are the authors referring here to aerosol composition, evolution of aerosol composition, gas-aerosol phase partitioning, or something else? Arguably, the types and strengths of major sources for primary and secondary aerosol constituents are more important drivers of "the aerosol phase" than LWC and pH.

Page 29,526, lines 2-3. This statement is potentially misleading. Direct "in situ" measurement of pH in minimally diluted extracts of sampled aerosol can be reliably extrapolated to aerosol solution pHs at ambient LWCs [e.g., Keene et al., 2002, GRL; 2004, JGR]. The text should be clarified.

Page 29,526, lines 11-14. Hennigan et al. [2014] showed that reliable estimates of aerosol solution pH based on the thermodynamic properties of compounds with pH-dependent solubilities require measurements of both gas- and particulate-phase concentrations. Model calculations based on "meticulous measurements" of aerosol composition alone do not yield reliable estimates of solution pH. The text should be clarified in this regard to minimize the potential for confusion.

Page 29,526, line 15. Most pH-dependent pathways involving the bioavailability of nutrients do not involve "catalytic" reactions. Suggest revising for clarity.

Page 29,526, last 3 lines. The relative importance of different pathways for SO2 oxidation is strongly pH dependent. The solubility of SO2 in aerosol solutions at pH less than 3 is quite low and, consequently, in the presence acidic aerosol in this pH range, most SO2 is oxidized in the gas phase [e.g., Keene et al., 1999, J. Aerosol Sci.] not via "heterogeneous" pathways as suggested by the authors. The text should be clarified.

Page 29,528, lines 8-16. Reliable estimation of LWC based on this approach requires that both nephelometers yield accurate results. Were the two instruments intercompared at the same RH to verify that results were directly comparable? The authors' approach also requires that particles pass at 100% efficiency through the drier. Was the passing efficiency of the dryer tested to verify that there were no significant line losses (e.g., to walls via electrostatic effects at low RH)? Finally, this approach requires that RH of 35% represents a reasonable threshold below which all aerosols effloresced. Was this verified via measurements at lower RH? Engelhart et al. [2011, ACP] report that aerosols at the Finokalia station can retain significant liquid water at RHs well below 35%. It would be helpful to report additional details regarding quality-assurance procedures that were employed for this component of that analysis or, if the above issues were not addressed experimentally, to state and justify the associated assumptions that were required.

Page 29,528, lines 17-19. It would be appropriate to specify the non-refractory constituents that were quantified by the ACMS and to report the associated detection limits. Since concurrent PM1 ionic compositions based on filter samples were measured in parallel, it would also be appropriate to mention the range in mass of refractory ionic constituents that were not characterized by the ACMS.

Page 29,528, lines 22-23. It would be helpful to specify the size cut of the critical aperture in the ACMS. Is it precisely 1-μm ambient diameter and, if not, what are the implications for comparison with results based on the PM1 filter samples?

Page 29,528, lines 28-28. The source for the "recommended collection efficiency" should be cited. It would also be appropriate to specify the constituents that were "verified by comparison" with the PM1 filter data, the number of paired observations that were compared, and the results of the comparisons (e.g., slopes, intercepts, and correlation coefficients for regressions of paired data).

Page 29,530, lines 18-19. It would be helpful to briefly address the range in magnitude of bias in the estimated mass introduced by ignoring refractory components other than BC (such as NaCl and non-ionic crustal constituents that are not quantified by the ACMS).

Page 29,532, first few lines. The methods used to collect and analyze the PM1 filter samples, the constituents that were measured, and the associated data quality should be reported in the methods section.

Page 29,533, lines 1-10. This approach is confusing. Reliable results based on ISORROPIA run in the "forward" mode require measurements of the total (gas + aerosol) concentrations of aerosol precursors in the air parcel. How can reliable model calculations be run in the forward mode when "gas-phase measurements of ammonia (NH3(g)) were generally not available?" In addition, there is no mention of NH3 measurements in the methods section. The measurement technique for NH3, frequency of measurement, and data quality should be reported. How often were simultaneous measurements of NH3 and NH4+ available? When the model was run in the "forward" mode for periods during which NH3 was not measured (i.e., most of the time), it appears that NH3 was initialized to 0.0 (i.e., NH3 + NH4+ was assumed to equal to NH4+). This important point should be stated explicitly. Do the calculated pHs reported by the authors include those for periods when NH3 was available and considered in the calculations together with those for periods when NH3 was not available and ignored in the calculations? If so, these results should be differentiated in some way since they

are not directly comparable.

As an alternative to estimating aerosol pH based on the phase partitioning of NH3, if measured during the campaign, pH could also be estimated based on the phase partitioning of HNO3 and/or HCl. Were gas-phase data available for either of these species?

The authors cite Guo et al. [2015] in support of the assumption that negative bias in calculated aerosol pH introduced by operating the model in the "forward" mode without NH3 data would be less than 1 pH unit (i.e., less than a factor of 10 in H+ concentration). However, based on an assumed ratio of NH3 to NH4+, the cited analysis by Guo et al. (Section 4.2.5) actually suggests a somewhat greater upper limit for potential bias (1.38 pH units) and that upper limit excludes any additional uncertainty introduced by the assumed ratio of NH3 to NH4+. Consequently, the actual upper limit for bias based of Guo et al. [2015] would be greater than 1.38 pH units. Simple thermodynamic calculations over a range NH3 mixing ratios reported in the literature also suggest that the likely upper limit for potential bias would be greater than 1.0 pH unit. In addition, results reported by Guo et al. correspond to the southeastern US, which represents a quite different chemical regime than that of the eastern coastal Mediterranean region so it is unclear that the potential magnitudes of inferred bias at the two locations are at all comparable. The authors could conduct a more credible error analysis by using their own data for the periods when NH3 data were available to evaluate the potential range in bias under the ambient conditions that existed during the campaign. For those periods, they could simply compare results for "forward"-mode model calculations initialized with total NH3 (NH3 + NH4+) versus paired results for those initialized with only the corresponding NH4+.

Based on the above, it appears that the inferred aerosol acidities reported by the authors are not representative or interpretable in terms of processes in the ambient atmosphere.

Figure 1. It is virtually impossible to interpret some components of this figure. Suggest partitioning into multiple panels with different scales or converting to a stacked format with all constituents on the same scale. When available, it would also be helpful depict the NH3 data.

Figure 2. This figure would be easier to read if converted to a stacked format on the same scale. Lines connecting the time series during breaks in sampling should be removed as they were in Figure 1. To facilitate direct comparison, it would also help to use identical X axes on Figures 1 and 2. Many of the data depicted in Figure 2 precede the start of the campaign noted in the Methods section (August). Do data depicted in other figures correspond to the time series depicted in Figure 1 or in Figure 2? Unless otherwise specified, all information reported in the manuscript should correspond to the same period. Is there some reason why the earlier period of record was excluded?

Page 29,536, line 15, page 29,537, lines 12 to 21, Page 29,538, lines 9-16, and elsewhere. The method used to calculate trajectories, identify "the geographical sector and/or source region," and to characterize "…air masses influenced by mineral dust and by biomass burning" should be described in the methods section. For example, what specific criteria were used to define dust events (page 29,538) based on "… large amounts of particulate matter and high concentrations of crustal ions …". On page 29,539, the authors state that only "weak" dust events were sampled so it's unclear how the relative "amounts of particulate matter" allowed these "weak" events to be differentiated from periods with relatively less dust. In addition, Ca2+ originates from both marine and crustal sources. The method used to differentiate the "crustal" contribution should be specified in the methods section. Since non-sea-salt concentrations of Ca2+ at marine-influenced sites often correspond to small differences between relatively much larger numbers, the associated uncertainties can be proportionately quite large and should also be reported and considered in the context of employing Ca2+ as a crustal tracer. A figure with a map depicting the trajectories, source regions, and/or transport probability fields for the categories listed in Table 1 would also be a

useful addition.

Page 29,537, line 2, Table 1, and elsewhere. Presumably, the reported "average … pH" and associated standard deviation correspond to the average and standard deviation for aqueous concentrations of H+ expressed as pH. If so, the text should be clarified. If not, both the results and the corresponding text should be revised accordingly. It is inappropriate to directly average lognormally distributed values such as pH.

Page 29,538, lines 6 to 8. If retained, the methods used to collect and analyze the PM10 filter samples and the associated data quality should be reported in the methods section. However, when chemically distinct aerosol size fractions of PM10 are sampled in bulk, the pH of the bulk mixture differs from that of (1) the relatively less acidic supermicron size fractions with which HNO3 and HCl partition preferentially and (2) the more highly acidic submicron size fractions with which NH3 partitions preferentially. Consequently, based on both observations and theory, it is evident that sampling PM10 aerosol in bulk drives artifact phase changes of compounds with pH-dependent solubilities and, thus, pHs inferred from such bulk data are not representative. Chemically conservative constituents of PM1 and PM10 samples can be reliably compared and interpreted but ionic constituents of compounds with pH-dependent solubilities (including H+, NO3-, Cl-, and NH4+) cannot. The text and Table 1 should be revised accordingly.

Page 29,539, line 1. "nss" is not defined, the method used to calculate nss-K is not described, no nss-K data are reported, and nss-K is not an acid or a base and, thus, has no direct influence on the acidity or alkalinity of the aerosol.

Page 29,539, line 23. Suggest adding a citation to support the statement that the eastern Mediterranean in "P limited."

Page 29,539, line 27. These results should be reported as "unpublished data" not cited as a manuscript in preparation.

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