Atmos. Chem. Phys. Discuss., 15, 29523–29554, 2015
www.atmos-chem-phys-discuss.net/15/29523/2015/
doi:10.5194/acpd-15-29523-2015

Response to Anonymous Referee #3 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.

Response: *We thank the reviewer for the well-articulated and thoughtful arguments that helped improving the presentation of our results, in particular the associated uncertainties and the manuscript as a whole. We have revised our manuscript in view of the reviewer's concerns and have shown that the pH estimates are reliable and with a constrained level of uncertainty and bias. We have further elaborated on these points in the revision for clarity. Below is a point-by-point response (in italics) to the comments raised by the reviewer.*

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.

Response: *Having the gas and aerosol phase measurements indeed provide the least uncertain pH estimates (Hennigan et al., 2015). However, using only aerosol-phase concentration in a forward partitioning calculation can still yield useful pH calculations (e.g., Guo et al., 2015). We evaluate whether this is the case in our data with two approaches: (i) when gas and aerosol data are available, we first test the ability of ISORROPIA-II to reproduce the observed partitioning of inorganic semi-volatiles; the same data are then used to quantify the shift in pH when gas-phase concentrations are omitted from the calculations. (ii) when gas-phase data are not available, thermodynamic calculations are carried out with the observed aerosol composition data in combination with climatological values of gas-phase species (NH_3 and others). The shift in aerosol pH between zero and high concentrations of gas-phase volatiles is then quantified as the upper limit in bias. Both methods are used in this study.*

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 method (i) described above was used to estimate the bias in the original submission. We have also used method (ii) to calculate another estimate in the bias and we find that the pH bias does not exceed one unit. Thus, based on these two approaches we can state that 1 pH unit is actually a generous estimate of the bias.

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.

Response: *We agree with the reviewer that the bias is not constant and that all coastal sites do not behave similarly. Our analysis of Finokalia data focuses primarily on the fine (PM1) fraction and shows that the thermodynamic model reproduces the ammonia partitioning when available, and that derived pH values are well within other pH studies for the fine fraction, including Keene et al. (2004). Finokalia PM1 aerosol contains a considerable amount of sulfates, that does not vary considerably with day for the whole time period considered in this study (June-November 2012; see figure below, also provided in the supplementary material). From long-term measurements of the aerosol -composition at the site, the relative contribution of the main PM$_1$ constituents, including ammonium, is quite consistent over the years (e.g., Mihalopoulos et al., 1997; Kouvarakis et al., 2001; Sciare et al., 2003; Koulouri et al., 2008, Bougiatioti et al., 2009; 2011; 2013). A fluctuation of 10-20% in sulfate and/or ammonium concentrations is not expected to be reflected in a pH change, given the logarithmic scale of the property. Given the above, the low concentration of other non-volatile ions (such as Na, K, etc.), and that we are far away from local sources that induce external mixing, the submicron aerosol at Finokalia is internally mixed, highly acidic, and varies slowly with time and hence in equilibrium with the gas phase. Similar conclusion that particles were internally mixed and liquid, has been reached by Hildebrandt (ACP, 2010) based on one month intensive observations with AMS at Finokalia in May 2008. Our findings also imply that the ammonia measurements available for the short period are representative of the whole studied period – as the NH$_4^+$ record does not indicate considerable fluctuations. Therefore, it is expected that ISORROPIA II is able to capture fine pH in our study, with a constrained level of uncertainty when not using gas-phase NH$_3$, that is estimated to be less than 1 unit of pH.*

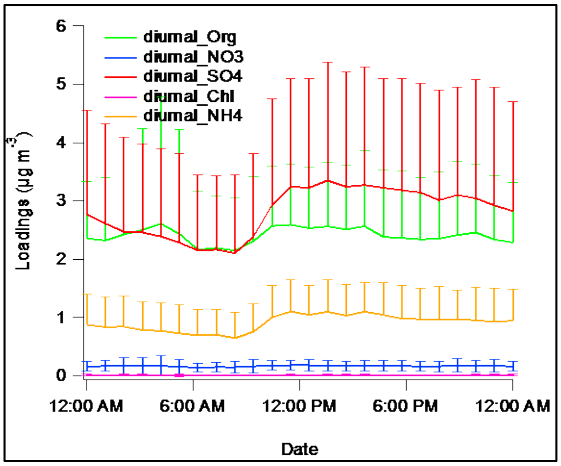

Figure S3: Mean diurnal variability of the main non-refractory aerosol constituents over the studied measurement period (Aug-Nov 2012).

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.

Response*: We thank the reviewer for pointing out this omission. Short descriptions about the wet annular denuder (WAD) for the gas phase measurements and the ion chromatography analysis are added in the instrumentation section. In addition, information on detection limits and precision for the various techniques applied here, is added in the revised text.*

The analysis is based primarily on the bulk, ionic composition of particles less than 1µm 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 super micron 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.

Response*: We agree with the reviewer that there is a strong link between aerosol pH and aerosol size distribution due to the chemical composition changes with changes in the aerosol size. However, by definition atmospheric aerosol science needs to consider population characteristics and thus is grouping atmospheric aerosols in size bins or in modes. Higher size resolution considered is leading to higher accuracy in the pH calculations. A comment in this respect has been added in the manuscript. We actually show that the acidity of the PM10 fraction is quite different from the acidity of the PM1. It will be also emphasized in the manuscript that* PM_{10} *pHs are qualitative, owing to the external mixing of the aerosol.*
Using the same acidity for PM1 and PM10 aerosols is wrong and would clearly lead to large biases in predicted nutrient solubility. However, it is not obvious that the nutrient flux from the fine mode is negligible either; the flux is certainly smaller than in the coarse mode – but it can transport much farther away from source regions before deposition, and be considerably more acidified (hence bioavailable). In reality the relative contributions of fine and coarse mode aerosol to the nutrient fluxes are best assessed by comprehensive atmospheric models that consider all the relevant processes from emission to deposition. These points are now better emphasized in the revised manuscript.

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.

Response*: The composition of particles less than 1 μm diameter are not subject to filter artifacts as it is provided by the ACSM, for the non-refractory submicron aerosol.* PM_1 *calculations are all based on ACSM measurements and respective* PM_1 *ionic concentrations for cations such as* Na^+, Ca^{2+}, Mg^{2+}, *corresponding to the fine fraction which is in equilibrium. Therefore, the corresponding submicron acidity is quantitative and succeeds in reproducing the partitioning of ammonia in the gas phase. We completely agree with the reviewer that, on the other hand, the* PM_{10} *results are less quantitative than the* PM_1 *results as obviously particles are not in equilibrium. We can still say however that the coarse mode pH is higher compared to the fine mode pH, especially during periods with a high sea-salt and dust influence. We will make it clear and emphasize it in the revised version of the manuscript.*

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.

***Response**: Amended. The text now reads "Particle water (LWC) and pH are important characteristics of the aerosol phase, impacting on heterogeneous chemistry…".*

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.

***Response**: The text has been rephrased **"**Direct measurements of aerosol pH "in situ" are challenging (e.g., Keene et al., 2002; 2004) and require careful considerations owing to the non-conserved nature of the hydronium ion and partial dissociation of inorganic and organic electrolytes in the aerosol. These challenges have led to the suggestion that indirect alternatives – such as measuring the semi-volatile partitioning of key species sensitive to pH, combined with comprehensive models may provide a reasonably accurate estimate of pH that can be carried out with routine measurements (Hennigan et al., 2015)…".*

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.

***Response**: Indeed, Hennigan et al. (2015) show that we need in general to know gas and aerosol phase concentrations for an accurate and unbiased pH calculation. However, if some uncertainty or a known level of pH bias can be tolerated, aerosol measurements alone can still be quite informative for determining the pH. This was demonstrated quite well in Guo et al. (2015) and is also the case here; we will make sure all these points are emphasized and clarified in the manuscript. See also our relevant reply to the first general comment of the reviewer.*

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

***Response:** Amended. The sentence now reads "Directly linked to aerosol pH and LWC is the bioavailability of nutrients contained within dust, involving pH-dependent catalyzed redox-reaction pathways".*

Page 29,526, last 3 lines. The relative importance of different pathways for SO_2 oxidation is strongly pH dependent. The solubility of SO_2 in aerosol solutions at pH less than 3 is quite low and, consequently, in the presence acidic aerosol in this pH range, most SO_2 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.

***Response**: The statement was within the context of cloudy atmospheres and the presence of coarse mode dust particles. For clarification, the sentence now reads "…and the subsequent acidification through heterogeneous oxidation of the* SO_2 *on deliquescent dust particles within the plume, Meskhidze et al. (2003) concluded that…".*

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.

***Response**: Since 2011 the Finokalia station has been part of the European Research Infrastructure for the observation of Aerosol, Clouds, and Trace gases (ACTRIS) (http://actris.eu/). Being part of ACTRIS requires that all participants fulfill certain requirements and comply with Standard Operating Procedures in order to ensure the quality of data reported to the EBAS database. Therefore, both nephelometers are sent once a year for intercomparison at the World Calibration Centre (WCC) for Physical Aerosol Properties at the Leibniz Institute for Tropospheric Research in Leipzig, Germany. Intercomparisons are performed with the operating dryers. The same instruments and configurations have also taken part in other measurement campaigns in the past e.g. Kalivitis et al., 2011; Pilinis et al., 2014. Based on the ISORROPIA model run for metastable ammonium sulfate aerosol at an RH of 30%, the maximum water which can be contained under these conditions is 1.21 $\mu g\ m^{-3}$, which is less than 12% of the total submicron aerosol mass. Finally, Guo et al. (2015) have demonstrated that any small amount of water that may be present in low RH, does not necessarily correspond to a high LWC bias, because the water uptake increases exponentially with RH.*

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.

***Response**: We thank the reviewer for this comment. Constituents quantified by the ACSM include organics, sulfate, ammonium, nitrate and chloride. Detection limits for all constituents for 30 min of averaging time are provided in detail in the publication of Ng et al. (2011) and are for ammonium, organics, sulfate, nitrate, and chloride are 0.284 $\mu g\ m^{-3}$, 0.148 $\mu g\ m^{-3}$, 0.024 $\mu g\ m^{-3}$, 0.012 $\mu g\ m^{-3}$, and 0.011 $\mu g\ m^{-3}$, respectively. Bougiatioti et al. (2014) provide a comparison between ACSM and PM_1 filter values for sulfate, ammonium and organics as well as mass from ACSM constituents + Black Carbon compared to SMPS measurements, for a large subset (16/08-30/09/2012) of the sampling period of the current dataset. This is now referred to in the revised manuscript.*

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 1µm ambient diameter and, if not, what are the implications for comparison with results based on the PM1 filter samples?

***Response**: The aerodynamic lens of the ACSM allows for the detection of particles up to 700 nm. For the main aerosol constituents, i.e. organics, sulfate and ammonium, the results between the comparison of the ACSM and PM_1 filter concentrations is provided by Bougiatioti et al. (2014) and will be referenced in the text.*

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).

Response*: Amended, both source of the recommenced collection efficiency as well as the results of the comparisons with PM_1 filter data are cited in the revised manuscript, as a reference from Bougiatioti et al. (2014) supplementary material, which is a large subset of the currently presented 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).

Response*: Based on the study by Koulouri et al. (2008) for a two-year period at the same sampling site, it has been demonstrated that for fine particles (in that case D_a<1.3 μm) the contribution of the marine factor to the total loadings was 10.2%. Similarly, dust contribution in the fine fraction can vary between 6 and 10% for summer and winter, respectively. Nevertheless, during the sampling period presented in the manuscript, as already mentioned, the masses derived from ACSM+BC observations and from SMPS observations are in very good agreement, therefore the bias introduced by ignoring refractory components other than BC is regarded as minimum.*

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.

Response*: Amended, a short description for the PM1 filters analysis by ion chromatography is added in the instrumentation section (Section 2.2).*

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 ($NH_{3(g)}$) were generally not available?"

Response: *This comment is related to the first general comment of the reviewer that has been addressed in our corresponding replies. Indeed the least uncertain pH estimates are provided when both aerosol and gas phase measurements are considered. However, the use of only aerosol-phase concentrations in the forward mode calculation can still result in useful pH calculations. A sensitivity test in order to prove this assumption is carried out by comparing (a) the reproducibility of partitioning of inorganic semi-volatiles and (b) the shifts in calculated pHs by combining aerosol composition data with climatological values of gas-phase species.*

In addition, there is no mention of NH_3 measurements in the methods section. The measurement technique for NH_3, frequency of measurement, and data quality should be reported. How often were simultaneous measurements of NH_3 and NH_4^+ available?

Response*: This is a good point. A short description about the wet annular denuder (WAD) for the gas phase measurements along with the time resolution and uncertainty of the measurements is added in the instrumentation section.*

When the model was run in the "forward" mode for periods during which NH_3 was not measured (i.e., most of the time), it appears that NH_3 was initialized to 0.0 (i.e., NH_3 & NH_4^+ was assumed to equal to NH_4^+). 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 NH_3 was not available and ignored in the calculations? If so, these results should be differentiated in some way since they are not directly comparable.

***Response**: As $NH_{3(g)}$ measurements were not available for the whole period, calculation runs were indeed performed with NH_3 & NH_4^+ assumed to equal to NH_4^+. This is now explicitly stated in the revised version of the manuscript.*

As an alternative to estimating aerosol pH based on the phase partitioning of NH_3, if measured during the campaign, pH could also be estimated based on the phase partitioning of HNO_3 and/or HCl. Were gas-phase data available for either of these species?

***Response**: The alternative proposed by the reviewer of estimating aerosol based on the phase partitioning of HNO_3 and/or HCl is not possible as the wet annular denuder (WAD) instrument was only connected to a cation chromatography system.*

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 NH_3 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 NH_3 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.

***Response**: In order to see the direct influence of not including the gas phase ammonia measurements in the pH calculation, we performed a sensitivity study by adding different amounts of gas phase ammonia to the system and quantifying the response in pH. Initial results of ISORROPIA, the ones that are reported in the manuscript were compared to results obtained after adding 0.5, 1.2, 3.2 and 5 $\mu g\ m^{-3}$ of ammonia. The values of 1.2 and 3.2 $\mu g\ m^{-3}$ were the median and maximum values of the gas phase measurements respectively. These values are also within the observed values reported by Guo et al. (2015). A lower value (0.5 $\mu g\ m^{-3}$) was also applied and finally 5 $\mu g\ m^{-3}$ was selected as an extreme value which is very close to the European critical level for NH_3, established to 8 $\mu g\ m^{-3}$ as an annual mean (Air Quality Guidelines for Europe, 2000). From a 3-year study conducted several years ago at the Finokalia station (Kouvarakis et al., 2001) it was seen that $NH_{3(g)}$ concentrations during summertime ranged from 0.02 to 1 $\mu g\ m^{-3}$ with a mean and median value of 0.32 and 0.28 $\mu g\ m^{-3}$, respectively, which is well below the maximum selected values for the sensitivity test. Therefore, based on climatology, neglecting the gas phase in the calculations has a difference of around 0.5 units in the pH (from 1.38 to 1.85 median values). The results of the sensitivity test are provided in the supplementary material (Figure S4) and below. Figure S4 shows the different pH median values with the 1st and 3rd percentile as derived for the different amounts of added ammonia. Error bars represent the upper and lower whiskers, derived from the 1st and 3rd percentile and the interquartile range (IQR). It can be seen that by adding even 5 $\mu g\ m^{-3}$ of ammonia, pH values differ by a maximum of 1 unit (1.4 vs 2.4), as already mentioned in the manuscript. It can also be seen from both figures that between the addition of 3.2 and 5 $\mu g\ m^{-3}$ of ammonia, the difference in pH is very small.*

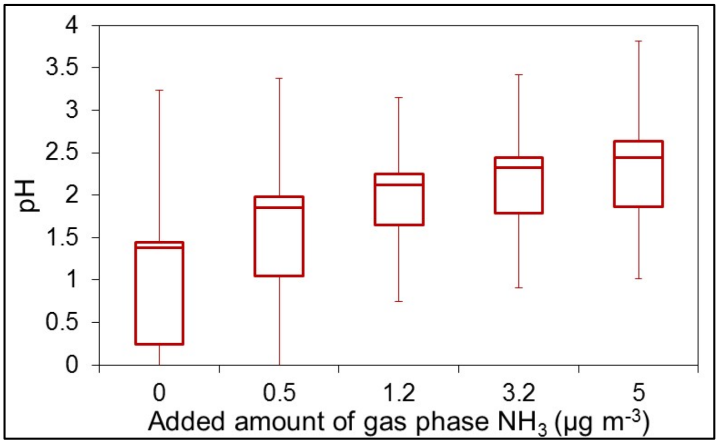

Figure S4: *Box plot depicting the median pH values calculated by ISORROPIA II for the different amounts of added gas phase ammonia. Error bars represent the upper and lower whiskers (Q_1-1.5*IQR and Q_3+1.5*IQR, respectively).*

The authors could conduct a more credible error analysis by using their own data for the periods when NH_3 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 NH_3 (NH_3 + NH_4^+) versus paired results for those initialized with only the corresponding NH_4^+.

Response*: We thank the reviewer for this suggestion that we have followed, performed such error analysis and incorporated it in the revised manuscript. For the subset of the analyzed dataset when both NH_3 as well as ammonium from the ACSM data were available, we directly compared the pH and LWC valued derived from ISORROPIA in the forward mode when calculations were initiated with total (NH_3+NH_4^+) versus paired results (n=328) for the respective ones initiated with only particulate phase NH_4^+. The results show that for the specific periods, the addition of NH_3 in the calculations has a minimum effect to both pH ($y=0.965x$, $R^2=0.584$) and LWC ($y=1.055x$, $R^2=0.993$). This finding is now shown and discussed in the corresponding section (Section 2.4) of the revised manuscript.*

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.

Response*: In our earlier replies to the reviewer, we have addressed the issues raised by the reviewer concerning the reported aerosol acidities and we argued /shown that the computed pH values are representative of the fine fraction of aerosols while this is not the case for the coarse aerosols.*

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 NH_3 data.

Response*: We agree with the reviewer that the readability of Figure 1 is not satisfactory. All reported data are for the period between June 8th and November 6th 2012. This will also be amended in the Methods section for the manuscript. Figure 1 will be converted to stacked format as proposed by the reviewer.*

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?

***Response**: We thank the reviewer for pointing this out. The inconsistency of the time series between Figures 1 and 2 is now addressed and all information reported in the manuscript corresponds to the same period (June 8th to November 6th 2012). Both Figures 1 and 2 are now converted to a stacked format to the same scale.*

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, Ca^{2+} 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 Ca^{2+} 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 Ca^{2+} 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.

***Response**: The model and the conditions used for the calculation of the back trajectories are now described in the methodology section. The specific criteria based on crustal ions are also described and the methodology of the ion chromatography is also added. "Weak" dust events refer to PM_{10} concentrations not exceeding 55 $\mu g\ m^{-3}$. Crustal calcium is calculated by subtracting the concentrations of sea-salt $Ca^{2+} = [Na]*0.038$ and dust concentration can be estimated from nss-Ca^{2+}. This methodology has been used successfully for mass closure studies at the site (Sciare et al., 2005) and this information has been added in the methodology section. From the back trajectory analysis, a representative plot for each category type listed in Table 1 has been added in the supplementary material.*

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.

***Response**: We kindly disagree here. Of course averaging of a non-linear metric, such as pH, would result in a biased value if we are considering mixing of samples into one volume that is allowed to react. Here, however, we are talking about temporal variability in aerosol properties; each time instant is independent from each other so averaging is acceptable.*

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 HNO_3 and HCl partition preferentially and (2) the more highly acidic submicron size fractions with which NH_3 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^+, NO_3^-, Cl^-, and NH_4^+) cannot. The text and Table 1 should be revised accordingly.

***Response**: Once more we would like to point out the fact that the PM_{10} results are just indicative and not quantitative as obviously coarse particles are not in equilibrium with the gas phase. This will be emphasized in the revised manuscript. Nevertheless, the take-home message we wanted to point out with Table 1 is the prevalence of the fine or of the coarse fraction water and the pH values for the different types of sources/regions.*

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.

***Response**: 'Nss' (Non-sea-salt) is now defined in the revised manuscript for clarity. Note however that the statement on nss-K is provided as an additional plausible reason found in the literature (Zhang et al. 2015 reference) why biomass burning aerosol exhibits higher pH values. It does not concern data from Finokalia station. No nss-K data are reported in our study, therefore no method to calculate nss-K is described. Non-sea-salt potassium (nss-K) is higher in air masses influenced by biomass burning (e.g. Zhang et al. 2015), and being an ionic species would partake in the pH calculations.*

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

***Response**: Good point. Done.*

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

***Response**: Done.*

References:

Bougiatioti, A., Fountoukis, C., Kalivitis, N., Pandis, S.N., Nenes, A., and Mihalopoulos, N.: Cloud condensation nuclei measurements in the marine boundary layer of the eastern Mediterranean: CCN closure and droplet growth kinetics, Atmos. Chem. Phys., 9, 7053-7066, 2009.

Bougiatioti, A., Nenes, A., Fountoukis, C., Kalivitis, N., Pandis, S.N., and Mihalopoulos, N.: Size-resolved CCN distributions and activation kinetics of aged continental and marine aerosol, Atmos. Chem. Phys., 11, 8791-8808, doi:10.5194/acp-11-8791-2011, 2011.

Bougiatioti, A., Zarmpas, P., Koulouri, E., Antoniou, M., Theodosi, C., Kouvarakis, G., Saarikoski, S., Mäkelä, T., Hillamo, R., Mihalopoulos, N.: Organic, elemental and water-soluble organic carbon in size segregated aerosols, in the marine boundary layer of the Eastern Mediterranean, Atmos. Environ., 64, 251-262, 2013.

Hennigan, C. J., Izumi, J., Sullivan, A. P., Weber, R. J., and Nenes, A.: A critical evaluation of proxy methods used to estimate the acidity of atmospheric particles, Atmos. Chem. Phys., 15, 2775– 2790, doi:10.5194/acp-15-2775-2015, 2015.

Hildebrandt, L., Engelhart, G.J., Mohr, C., Kostenidou, E., Lanz, V.A., Bougiatioti, A., DeCarlo, P.F., Prevot, A.S.H., Baltensperger, U., Mihalopoulos, N., Donahue, N.M., and Pandis, S.N.: Aged organic aerosol in the Eastern Mediterranean: the Finokalia Aerosol Measurement Experiment-2008, Atmos. Chem. Phys., 10, 4167-4186, 2010.

Guo, H., Xu, L., Bougiatioti, A., Cerully, K.M., Capps, S.L., Hite, J.R., Carlton, A.G., Lee, S.-H., Bergin, M.H., Ng, N.L., Nenes, A., and Weber, R.J.: Particle water and pH in the southeastern United States, Atmos. Chem. Phys., 15, 5211-5228, doi:10.5194/acp-15-5211-2015, 2015.

Kalivitis, N. Bougiatioti, A., Kouvarakis, G., and Mihalopoulos, N.: Long term measurements of atmospheric aerosol optical properties in the Eastern Mediterranean, Atmos. Res., 102, 351-357, 2011.

Keene, W.C., Pszenny, A.A.P., Maben, J.R., Stevenson, E., Wall, A.: Closure evaluation of size-resolved aerosol pH in the New England coastal atmosphere during summer, J. Geophys. Res., 109, D23307, doi:10.1029/2004JD004801, 2004.

Keene, W. C., A. A. P. Pszenny, J. R. Maben, and R. Sander: Variation of marine aerosol acidity with particle size, Geophys. Res. Lett., 29(7), doi:10.1029/2001GL013881, 2002.

Koulouri E., S. Saarikoski, C. Theodosi, Z. Markaki, E. Gerasopoulos, G. Kouvarakis, T. Mäkelä, R. Hillamo, N. Mihalopoulos: Chemical composition and sources of fine and coarse aerosol particles in the Eastern Mediterranean, Atmospheric Environment, Volume 42, Issue 26, 6542-6550, 2008.

Kouvarakis, G. Mihalopoulos, N., Tselepides, T., Stavrakakis, S.: On the importance of atmospheric nitrogen inputs on the productivity of Easter Mediterranean, Global Biochem. Cycles, 15, 805-818, 2001.

Krom, M.D., Kress, N., Brenner, S., and Gordon, L.I.: Phosphorus limitation of primary productivity in the eastern Mediterranean Sea, Limnol. Oceanogr., 36 (3), 424-432, 1991.

Mihalopoulos N., Stephanou E., Pilitsidis S., Kanakidou M., Bousquet P.: Atmospheric aerosol composition above the Eastern Mediterranean region, Tellus, 49B, 314-326, 1997.

Pilinis, C., Charalampidis, P.E., Mihalopoulos, N., Pandis, S.N.: Contribution of particulate water to the measured aerosol optical properties of aged aerosol, Atmos. Environ., 82, 144-153, 2014.

Sciare J., H. Bardouki, C. Moulin, and N. Mihalopoulos: Aerosol sources and their contribution to the chemical composition of aerosols in the Eastern Mediterranean Sea during summertime, Atmos. Chem. Phys., 3, 291-302, 2003.

Sciare, J., Oikonomou, K., Cachier, H., Mihalopoulos, N. Andreae, M.O., Maenhaut, W., and Sarda-Estève, R.: Aerosol mass closure and reconstruction of the light scattering coefficient over the Eastern Mediterranean Sea during the MINOS campaign, Atmos. Chem. Phys., 5, 2253-2265, 2005.