Response to Reviewer Comments for "Urban aerosol chemistry at a land-water transition site during summer – Part 2: Aerosol pH and liquid water content" by Michael A. Battaglia Jr. et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-368-RC1, 2021"

We thank the reviewers for their detailed and helpful comments. We have addressed each comment with the Referee comments in bold and our reply in plain text immediately below. We provide at the end the edited manuscript with all changes highlighted.

REVIEWER #1

Major Comments

1.) ***It looks necessary to quantify the impact of measurement uncertainties to these two pH calculation methods. The authors should also provide the QA/QC information, not only limited to concentrations, but also the impact on possible ranges of pH calculated.***

We have attempted to address this issue by referring readers to the literature. Additional discussion of the impact on calculated aerosol pH based on uncertainty in the measured input concentrations have been added. The following discussion was added at the conclusion of the Methods section of the paper to elaborate on these uncertainties:

"Commonly, a reasonable estimate of measurement errors associated with the species of interest are on the order of 15% + 1 nmol m^{-3} for online sampling methods (Murphy et al. 2017). Utilizing this estimate in the extreme acidic case (ambient observed SO_4^{2-} and NO_3^- adjusted to + 15% + 1 nmol m^{-3}; NH_4^+ adjusted to – 15% – 1 nmol m^{-3}) or non-acidic case (SO_4^{2-} and NO_3^- adjusted down by – 15% – 1 nmol m^{-3} and NH_4^+ adjusted up by + 15% + 1 nmol m^{-3}), the uncertainty of aerosol pH was predicted to vary by 0.1 – 1 pH units (Murphy et al. 2017). Similarly, Pye et al. (2020) reported that in cases for RH above 60% deviations of the ISORROPIA-predicted pH and the IUPAC-defined pH are less than one pH unit. The present calculations have similar uncertainties in the pH calculations."

2.) ***Line 107-108: Is it because how pH was defined (e.g. pH_c or pH_m in Jia et al. (2018))? It's better to clarify how the pH was defined in the first place.***

This statement has been clarified to reflect that the methods of Hennigan et al. 2015 and Zheng et al. 2020 are identical with the exception of the values of the equilibrium constants used. Based on our investigation, the non-ideality corrections introduced in Zheng et al. 2021 appear to be working towards ISORROPIA, but instead of calculating activity coefficients they interpolate with thermodynamic outputs from ISORROPIA (or E-AIM if desired) to try to mimic the thermodynamic models based on what they say impacts non-ideality the most (they base it on T, RH, and NO_3^-). The text has been updated to read:

"The method of Zheng et al. (2020) is based upon a similar approach in prior studies (Hennigan et al., 2015; Keene et al., 2004); the two methods are identical, with the minor differences a result of equilibrium constant values used based on ranges provided in the literature."

3.) ***Line 153: Looks like the authors intend to make comparisons of pH in different locations and discuss the influence from RH and T, but I did not see such discussions in the following discussion. I think the authors should clarify what "strong implications" they are referring to.***

The differences between locations were intended to describe the changes in diurnal T, RH, and ALWC between the Baltimore (urban) and HMI sites. The unique character of these profiles at the HMI site (neither strongly urban nor rural) was investigated as a driver of the model-predicted aerosol pH during the OWLETS 2 study. The discussion points have been linked together, and the original statement on Line 153 has been changed to read:

"The differences shown in Fig. 1 were due to the proximity of HMI to the Chesapeake Bay and have several implications for aerosol pH, which will be discussed in detail below."

4.) ***Line 162-171: NH3 phase partitioning also strongly depends on the availability of accompanied acids. Without balance ions, NH3 alone cannot form particles. On the other hand, for pure ammonium sulfate, the evaporation tendency of NH3 is also quite limited. Low concentrations of particulate acids could also lead to ammonia-rich atmosphere.***

We have attempted to address this comment together with Reviewer 2 Major Comment #2. Please see the response to Reviewer 2 Major Comment #2 for details.

5.) ***Figure 4 &5: These two figures provide valuable local information about pH response and of high importance for similar studies comparison. As a result, the authors should provide a more complete description about how the data points are chosen, averaged or processed. The authors have 20-minutes resolution data, while only 8 points are plotted. How were the bins chosen and why not just use all the measured data?***

Figures 4 and 5 have been expanded to display both the binned data (from the original manuscript) together with the entire collection of raw unbinned data used to generation the original figures to show any relevant trends. We have clarified the binning process by describing the maximum number of points permitted in each bin by addition of the following text to the figure captions:

"**Figure 4:** Relationship between aerosol pH and (a) temperature, (b) aerosol liquid water, and (c) total NH_3 (Tot-NH_3 = NH_3 + NH_4^+). Symbols represent mean values while error bars represent standard deviations; bins were limited to a maximum of 160 points per bin."

"**Figure 5:** Relationship between NH_3 partitioning (ε_{NH3} = NH_3/(NH_3 + NH_4^+)) and aerosol liquid water. Symbols represent mean values while error bars represent standard deviations,; bins were limited to a maximum of 160 points per bin."

6.) ***Line 225-231: Either high RH or high particle mass loading can be responsible for high ALWC, while it's hard to say the later case corresponds to the dilution effect. Could the authors distinguish which one dominates the ALWC? In the latter discussion, the authors mentioned the particles were likely externally mixed, so that the ALWC involved in the NH_3 phase partitioning processes should be, more or less, overestimated. Should that be considered here as well?***

Reviewer 2 expressed a related sentiment in Minor Comment #5 (Lines 228-240 of the original manuscript). While the additional discussion of that comment addresses, more specifically the surprising result of seemingly contradictory findings on relatively invariant pH with both

increasing NH_3 and ALWC, we have also added clarifying statements to address this comment as well. The following comment has been added at the end of line 227 of the original manuscript:

"A combination of particle mass loading, aerosol composition, and ambient RH are responsible for the variations in ALWC."

Additionally, it should be noted that previous studies have shown that the ALWC predictions of aerosol thermodynamic equilibrium models are highly accurate. For example, Guo et al. (2015) observed excellent agreement between model-predicted ALWC and direct observations during the SOAS campaign. This is one of the key parameters evaluated when a new model is published (e.g., Fountoukis and Nenes, 2007). This is further supported by the results of Ansari and Pandis (1999), who found generally excellent agreement in ALWC predictions between four different thermodynamic equilibrium models, even when predictions of other semivolatile species did not agree.

<u>Minor Comments</u>

1.) Introduction: it's better to mention some current existing methods of pH direct Measurement.

We have added the following discussion regarding the existing method of aerosol pH direct measurement:

"However, direct measurements of aerosol pH remain challenging. Single particle studies of aerosol pH using Raman spectroscopy have been performed, but are limited by the presence of both HSO_4^- and SO_4^- limiting their application to more acidic particles (Boyer et al., 2020; Rindelaub et al., 2016). Colorimetric measurements of aerosol pH have also been employed, but such techniques have been limited to laboratory studies with relatively simple aerosol compositions (Craig et al., 2018; Jang et al., 2020)."

2.) Line 49: I do not follow the logic here, how does the previous sentence explain the later?

The sentences were intended to be linked based on the controlling regimes of NH_3 influence on aerosol pH, *i.e.*, the compositionally-controlled or meteorologically-controlled. The statements have been linked and clarified in the following manner and the text now reads:

"NH_3 partitioning is controlled by the concentration of strong acids and by the ambient temperature and relative humidity, hence, the dependence of pH on both composition and meteorology (Zheng et al., 2020). In some regimes, the meteorological factors are more important than the compositional factors, explaining why NH_3 can exist partially in the gas phase even when the aerosol pH is highly acidic (Nenes et al., 2020; Weber et al., 2016)."

3.) Figure 7: Should the relative concentrations of nitrate be more reflective to the Cl displacement extent than absolute concentrations? And on this Figure, about half the data points have Cl:Na >1, what's the possible explanation?

We do not feel that the relative concentrations of nitrate are more reflective to the Cl displacement extent than absolute concentrations. The additional components of sampled PM mass may have effects on the relative concentrations, but are unlikely to play a part in the actual displacement reaction. Regarding the Cl:Na > 1 condition present, our expectation is that there is an additional source of Cl that is difficult to account for, such as combustion sources from the similar industrial point sources documented in the Part 1 manuscript, local boat traffic, or equipment and truck traffic associated with work activities on Hart-Miller Island. Because we do not have a way to identify the additional Cl source, such discussion would be speculative.

REVIEWER #2 RESPONSES

Major Comments

1.) ***Given the poor performance of ISORROPIA for NH3 partitioning predictions (pH dependent) in this study, Eq. 1-Eq. 3 was used to calculate aerosol pH, and the pH calculated from these equations was significantly different from the ISORROPIA-predicted aerosol pH. However, these equations are for ideal conditions (without considering ion activity coefficients), and the non-ideality in aerosols can introduce deviations from the ideal conditions. Zheng et al. (https://doi.org/10.5194/acp-2021-55) has recently introduced a non-ideality correction factor for using these equations to calculate aerosol pH, and the aerosol pH calculated from the non-ideality corrected equations agreed well with the pH value determined by ISORROPIA.***

    Therefore, I suggest the authors to use the non-ideality corrected equations (either with non-ideality correction factor or with the related ion activity coefficients) to calculate aerosol pH and then compare with ISORROPIA predicted pH.

In Zheng et al. (2021), the goal is to account for non-idealities in the thermodynamic calculation of pH based on ammonia partitioning. Note that Zheng et al. (2020) performed their calculations assuming ideal conditions. The non-ideality treatment of Zheng et al. (2021) is not actually thermodynamic model output, but is estimated based on three factors that are determined to impact non-ideality: temperature, RH, and the fraction of particulate anions contributed by nitrate nitrate. The estimation occurs then by interpolating from tables generated from thermodynamic models like ISORROPIA and E-AIM.

This correction was carried out on our data here. The ISORROPIA-generated thermodynamic lookup tables were used and the pH_f (partitioning, non-ideal) were calculated and compared to the pH_f (partitioning, ideal). While the non-ideality correction increases the correlation with ISORROPIA-calculated pH, we chose to not include it for three reasons: (1) the correction is based on interpolation from ISORROPIA outputs and attempts to mimic its output with more computational efficiency that running the full model; however, we do not need to mimic

ISORROPIA, as we have all of the necessary inputs and have already run it in full. We use the ammonia partitioning method as a completely independent thermodynamic calculation. That being said, we acknowledge that the method used here is based on an ideal assumption (the same assumption of ideality used throughout Zheng et al., Science, 2020). (2) The absolute impact on the pH calculated is not severe and does not impact the conclusions of the work (on average, a difference of ~0.5 pH units between partitioning ideal and partitioning non-ideal was observed). (3) Finally, we appreciate the Referee's comment and alerting us to this very recent manuscript. Given that Zheng et al. (2021) is currently under review, we feel that it would be premature to adopt their methodology before it has passed the peer-review process. If substantial changes in their manuscript occur during revision (or if the manuscript is not accepted for publication), this would have serious implications for our conclusions if we adopt their methodology.

2.) ***Fig. 4, shows the relationship between aerosol pH and factors such as temperature, aerosol liquid water and total NH3. It seems that the influence of one factor on pH can also be affected by other factors. Is it possible to vary one factor with fixed other factors to investigate the influence of one factor?***

Pye *et al.* (2020) address this question in Table S3 of the accompanying supplemental information. For five aerosol thermodynamic equilibrium models (E-AIM model III, AIOMFAC-GLE, MOSAIC, ISORROPIA II, and EQUISOLV II, the authors make predictions of molality-based pH and related properties for the water + $(NH_4)_2SO_4$ + H_2SO_4 + NH_3 system at 298.15 K. For the case of their 'moderately acidic' water-free input system, increasing RH from 40% to 99% was demonstrated to increase ISORROPIA II-predicted aerosol pH from 1.84 to 4.47, with a corresponding change in the hydronium ion activity coefficient. For the 'highly acidic' water-free composition input (50% $(NH_4)_2SO_4$ by mass, with less NH_3), similar change in RH resulted in aerosol pH increasing from -0.15 to 2.54.

While this experiment was performed with idealized systems, as described in the main body of their manuscript, we would expect similar findings with our observational results, *e.g.* increasing RH would increase aerosol pH at fixed concentration, and increasing the acidic components of

the aerosol would decrease aerosol pH for fixed RH. However, doing so for our observations may not have much meaning, as ambient T, RH, and aerosol composition are fixed inputs at each time point for model inputs to predict aerosol pH.

Additionally, Tao and Murphy (2021), and Zhou et al. (2021), demonstrated the effects of individual drivers of aerosol pH on both diurnal and monthly/seasonal time frames utilizing ambient data by systematically decomposing the pH calculation. In most cases, temperature was the single largest driver, followed by NH_3 concentration, ambient RH, and aggregate particle properties in decreasing order of effect. Tao and Murphy (2021) found that temperature was the single largest driver of pH, followed by (in decreasing order of effect) the NH_3 effect (opposite the T effect), RH, and particle properties in Toronto, Canada. Likewise Zhou et al. (2021) found that temperature was the primary driver, both across seasons and day/night cycles, followed (generally) by the NH_x effect, then RH and occasionally SO_4^{2-}, and during certain periods of the diurnal cycle, the NVC effect in decreasing order of effect.

<u>Minor Comments</u>

1.) ***In Fig. S4, it would be better to use the same y scale when comparing pH values determined from different methods.***

We have combined the axes of the plots, ensuring the scales on the figure are identical for better comparison of the pH values.

2.) ***Line 228-240: "The result shown in Fig. 4b is somewhat surprising because NH3 partitioning was quite sensitive to ALWC (Fig. 5); the relatively invariant aerosol pH is unexpected given the increase in NH3 uptake in the presence of ALW." A discussion of this surprising result would be useful. (The following discussion in the manuscript about the dry deposition is not very relevant to this result).***

We have retained the discussion on dry deposition, as we feel it is valuable to the overall discussion of aerosol pH (though not necessarily to the point we intend to make), but we have added additional discussion related to the surprising result as requested by the reviewer. The following discussion has been added to elaborate on the point we intended to make:

"With increasing NH_3 uptake in the presence of, and simultaneous with, the increased ALWC, it would be anticipated that aerosol pH would become more basic both through the reaction of NH_3 to form NH_4^+ and due to the dilution effect of liquid water. However, the results of Figures 4 and 5 reveal that despite both the increase in NH_3 uptake and increase ALWC, aerosol pH remains relatively unchanged, with only a 0.5 pH unit change at the highest values of ALWC."

This change also contains additional clarification to address Reviewer 1 Major Comment #6 as described above.

3.) ***Line 296-298: ISORROPIA didn't give good NH3 partitioning predictions in this study and the different chemical compositions of the coarse- and fine-mode particles were used to explain it. I think the explanation is reasonable, however, I was still wondering what result you will get with E-AIM calculations. If the E-AIM also fails to predict NH3 partitioning here, this explanation would be more solid since E-AIM also assumes an internally mixed aerosol distribution.***

Making comparisons of ISORROPIA and E-AIM calculations is outside the scope of this particular work, and would be repeating work performed in recent studies. Notably, Pye et al. (2020) comprehensively compared multiple aerosol thermodynamic equilibrium models for consistency. In polluted environments, such as Mexico City, aerosol pH predictions obtained from E-AIM, ISORROPIA, and the NH_3 partitioning approach were shown to be in good agreement. Under both the moderately and highly acidic conditions described in Pye et al. (2020), E-AIM and ISORROPIA predicted values never exceeded 1 pH unit difference, and then only at low (<50% RH) values; for values above 60% RH this difference was on the order of 0-0.5 pH units. Exact values are given in Table 6 of Pye et al. (2020).

The pH of coarse-mode particles is anticipated to be higher than for fine-mode particles owing to the enrichment of the coarse-mode with NVCs from dust and sea salt. Differences of up to 4 pH units have been shown between fine- and coarse-modes. As E-AIM and ISORROPIA are shown to be in acceptable agreement at the observed ambient RH ranges in the present study (RH > 60%), it should be expected that ISORROPIA would more accurately predict the aerosol pH

when the coarse mode is included from an internally-mixed standpoint as E-AIM lacks NVC constituents as inputs.

References

Ansari, S. & Spyros N. Pandis (1999). An Analysis of Four Models Predicting the Partitioning of Semivolatile Inorganic Aerosol Components, Aerosol Science and Technology, 31:2-3, 129-153.

Boyer, H. C., Gorkowski, K., & Sullivan, R. C. (2020). In Situ pH Measurements of Individual Levitated Microdroplets Using Aerosol Optical Tweezers. *Analytical Chemistry*, *92*(1), 1089-1096. https://doi.org/10.1021/acs.analchem.9b04152

Craig, R. L., Peterson, P. K., Nandy, L., Lei, Z., Hossain, M. A., Camarena, S., Dodson, R. A., Cook, R. D., Dutcher, C. S., & Ault, A. P. (2018). Direct Determination of Aerosol pH: Size-Resolved Measurements of Submicrometer and Supermicrometer Aqueous Particles. *Analytical Chemistry*, *90*(19), 11232-11239. https://doi.org/10.1021/acs.analchem.8b00586

Fountoukis, C. and Nenes, A.: ISORROPIA II: a computationally efficient thermodynamic equilibrium model for K^+–Ca^{2+}–Mg^{2+}–NH_4^+–Na^+–SO_4^{2-}–NO_3^-–Cl^-–H_2O aerosols, Atmos. Chem. Phys., 7, 4639–4659, https://doi.org/10.5194/acp-7-4639-2007, 2007.

Hennigan, C. J., Izumi, J., Sullivan, A. P., Weber, R. J., & Nenes, A. (2015). A critical evaluation of proxy methods used to estimate the acidity of atmospheric particles. *Atmos. Chem. Phys.*, *15*(5), 2775-2790. https://doi.org/10.5194/acp-15-2775-2015

Jang, M., Sun, S., Winslow, R., Han, S., & Yu, Z. (2020). In situ aerosol acidity measurements using a UV–Visible micro-spectrometer and its application to the ambient air. *Aerosol Science and Technology*, *54*(4), 446-461. https://doi.org/10.1080/02786826.2020.1711510

Keene, W. C., Pszenny, A. A. P., Maben, J. R., Stevenson, E., & Wall, A. (2004). Closure evaluation of size-resolved aerosol pH in the New England coastal atmosphere during summer. *J. Geophys. Res.-Atmos.*, *109*(D23), D23307, Article D23307. https://doi.org/10.1029/2004jd004801

Nenes, A., Pandis, S. N., Weber, R. J., & Russell, A. (2020). Aerosol pH and liquid water content determine when particulate matter is sensitive to ammonia and nitrate availability. *Atmos. Chem. Phys.*, *20*(5), 3249-3258. https://doi.org/10.5194/acp-20-3249-2020

Rindelaub, J. D., Craig, R. L., Nandy, L., Bondy, A. L., Dutcher, C. S., Shepson, P. B., & Ault, A. P. (2016). Direct Measurement of pH in Individual Particles via Raman Microspectroscopy and Variation in Acidity with Relative Humidity. *J. Phys. Chem. A*, *120*(6), 911-917. https://doi.org/10.1021/acs.jpca.5b12699

Weber, R. J., Guo, H., Russell, A. G., & Nenes, A. (2016). High aerosol acidity despite declining atmospheric sulfate concentrations over the past 15 years [Letter]. *Nature Geoscience*, *9*(4), 282-285. https://doi.org/10.1038/ngeo2665

Zheng, G., Su, H., Wang, S., Andreae, M. O., Pöschl, U., & Cheng, Y. (2020). Multiphase buffer theory explains contrasts in atmospheric aerosol acidity. *Science*, *369*(6509), 1374. https://doi.org/10.1126/science.aba3719

Zheng, G., Su, H., Wang, S., Pozzer, A., and Cheng, Y.: Impact of non-ideality on reconstructing spatial and temporal variations of aerosol acidity with multiphase buffer theory, Atmos. Chem. Phys. Discuss. [preprint], https://doi.org/10.5194/acp-2021-55, in review, 2021.

Urban aerosol chemistry at a land-water transition site during summer – Part 2: Aerosol pH and liquid water content

M. A. Battaglia, Jr.[1,a], N. Balasus[1], K. Ball[1], V. Caicedo[2], R. Delgado[2], A. G. Carlton[3] , and C. J. Hennigan[1*]

[1]Department of Chemical, Biochemical, and Environmental Engineering, University of Maryland, Baltimore County

[2]Joint Center for Earth Systems Technology, University of Maryland, Baltimore County

[3]Department of Chemistry, University of California, Irvine

[a]Current affiliation: School of Earth and Atmospheric Sciences, Georgia Institute of Technology

Correspondence: C. J. Hennigan (hennigan@umbc.edu)

Abstract

Particle acidity (aerosol pH) is an important driver of atmospheric chemical processes and the resulting effects on human and environmental health. Understanding the factors that control aerosol pH is critical when enacting control strategies targeting specific outcomes. This study characterizes aerosol pH at a land-water transition site near Baltimore, MD during summer 2018 as part of the second Ozone Water-Land Environmental Transition Study (OWLETS-2) field campaign. Inorganic fine mode aerosol composition, gas-phase NH_3 measurements, and all relevant meteorological parameters were used to characterize the effects of temperature, aerosol liquid water (ALW), and composition on predictions of aerosol pH. Temperature, the factor linked to the control of NH_3 partitioning, was found to have the most significant effect on aerosol pH during OWLETS-2. Overall, pH varied with temperature at a rate of -0.047 K^{-1} across all observations, though the sensitivity was -0.085 K^{-1} for temperatures > 293 K. ALW had a minor

effect on pH, except at the lowest ALW levels (< 1 μg m^{-3}) which caused a significant increase in aerosol acidity (decrease in pH). Aerosol pH was generally insensitive to composition (SO_4^{2-}, SO_4^{2-}:NH_4^+, Tot-NH_3 = NH_3 + NH_4^+), consistent with recent studies in other locations. In a companion paper, the sources of episodic NH_3 events (95th percentile concentrations, NH_3 > 7.96 μg m^{-3}) during the study are analyzed; aerosol pH was higher by only ~0.1-0.2 pH units during these events compared to the study mean. A case study was analyzed to characterize the response of aerosol pH to nonvolatile cations (NVCs) during a period strongly influenced by primary Chesapeake Bay emissions. Depending on the method used, aerosol pH was estimated to be either weakly (~0.1 pH unit change based on NH_3 partitioning calculation) or strongly (~1.4 pH unit change based on ISORROPIA thermodynamic model predictions) affected by NVCs. The case study suggests a strong pH gradient with size during the event and underscores the need to evaluate assumptions of aerosol mixing state applied to pH calculations. Unique features of this study, including the urban land-water transition site and the strong influence of NH_3 emissions from both agricultural and industrial sources, add to the understanding of aerosol pH and its controlling factors in diverse environments.

1 Introduction

The acidity, or pH, of atmospheric aerosols affects the chemical and physical properties of airborne particles, and thus, their impacts on climate and health (Pye et al., 2020). The gas-particle partitioning of semi-volatile acidic and basic compounds – notably NH_3, HNO_3, HCl, and organic acids – depends in part on aerosol pH, which directly affects the particulate matter (PM) mass concentration (Nenes et al., 2020). The solubility of many particulate components is pH-dependent, including metals and nutrients, with implications for particle toxicity and nutrient deposition to ecosystems (Fang et al., 2017; Kanakidou et al., 2016). The optical properties of light-absorbing organic compounds, known as brown carbon, can exhibit a strong pH-dependence, which directly affects their climate impacts (Phillips et al., 2017). However, direct measurements of aerosol pH remain challenging. Single particle studies of aerosol pH using Raman spectroscopy have been performed, but are limited by the presence of both HSO_4^- and SO_4^- limiting their application to more acidic particles (Boyer et al., 2020; Rindelaub et al., 2016). Colorimetric measurements of aerosol pH have also been employed, but such techniques have been limited to laboratory studies with relatively simple aerosol compositions (Craig et al., 2018); (Jang et al., 2020). Given the importance of aerosol pH for atmospheric processes and the limitation in estimating acidity with proxies (e.g., ion balances), there has been increased effort in recent years to identify the factors that affect pH and to characterize temporal and spatial variations in the atmosphere (Hennigan et al., 2015).

Globally, aerosol pH is often quite acidic due to the ubiquity and abundance of strong acids like H_2SO_4, HNO_3, and HCl (Pye et al., 2020). Ammonia (NH_3) is unique among species that affect pH because it is the most abundant basic compound in the atmosphere. NH_3 partitioning is controlled by the concentration of strong acids and by the ambient temperature

and relative humidity, hence, the dependence of pH on both composition and meteorology (Zheng et al., 2020). In some regimes, the meteorological factors are more important than the compositional factors, explaining why NH_3 can exist partially in the gas phase even when the aerosol pH is highly acidic (Nenes et al., 2020; Weber et al., 2016). Due to its abundance and semi-volatile properties, NH_3 was identified as the most important buffering agent in aerosols across locations with diverse emissions, composition, and climatology (Zheng et al., 2020). In single-phase aqueous particles, organic compounds have a minor effect on pH (Battaglia Jr et al., 2019), though this is not the case for particles that have undergone liquid-liquid phase separation (Pye et al., 2018). Non-volatile cations (NVC) typically contribute a minor fraction of PM mass but can be critical for accurate predictions of pH, especially if NVC concentrations are overestimated (Vasilakos et al., 2018). Globally, NVC are most important in regions heavily impacted by dust emissions (Pye et al., 2020), but have minor effects on pH in other regions (Tao & Murphy, 2019; Zheng et al., 2020).

Aerosol pH is also strongly affected by meteorological factors. Equilibrium constants, including those that determine the gas-particle partitioning and aqueous dissociation of semi-volatile acids and bases, are temperature dependent. Temperature is a dominant factor driving variability in the seasonal and diurnal cycling of pH (Guo et al., 2015; Tao & Murphy, 2019). Temperature gradients, as occur in and around urban areas, can also drive large differences in pH, even if the composition is uniform over the same scales (Battaglia et al., 2017). Relative humidity (RH) regulates aerosol liquid water content (ALWC), which affects the partitioning of soluble gases and aqueous phase solute concentrations. ALWC may be the most important factor responsible for large pH differences observed between the southeast US (pH ~0.5-1.0) and the heavily polluted North China Plain (pH ~4-5), the two regions where pH has been most

extensively studied to-date (Zheng et al., 2020). These effects can be complex, or even partially offset. For example, an increase in temperature reduces pH owing to the shift in NH_3 partitioning towards the gas phase, but NH_3 emissions increase with temperature as well, producing an increase in pH and partially offsetting the pH changes due to temperature (Tao, 2020). More research is needed to better understand how all these factors together affect pH, and how this changes geographically and temporally.

In this study aerosol pH was characterized during the summertime (4 June to 5 July, 2018) at a land-water transition site near a large urban area (Baltimore, MD) as part of the OWLETS-2 (second Ozone Water-Land Environmental Transition Study) field campaign. This site is unique because meteorological phenomena, such as the bay breeze, affect pollution dispersion and recirculation (Loughner et al., 2014). Baltimore is impacted by different regional emission sources, as it is located in the populous and heavily trafficked I-95 corridor, downwind of the Ohio River Valley (He et al., 2013), and relatively close to regional agricultural operations that emit large amounts of NH_3 (Pinder et al., 2006). In a companion paper, the local sources of NH_3 during the OWLETS-2 study were examined, including an analysis of transient events with unexpectedly high NH_3 concentrations (Balasus et al., 2021). In this study, the effects of the observed NH_3 concentrations (including the aforementioned transient concentrations of unexpectedly high values), in combination with the unique meteorological phenomena associated with the land-water transition, on ALW and aerosol pH were investigated.

2 Methods

The OWLETS-2 study was conducted to characterize effects of meteorological phenomena associated with the land-water transition on summertime air quality in Baltimore.

Hart-Miller Island (HMI, coordinates 39.2421°, -76.3627°), a site located on the Chesapeake Bay ~10 km east of downtown Baltimore, hosted many of the ground-based measurements during the study (Fig. S1). Semi-continuous measurements of aerosol inorganic chemical composition and gas-phase NH_3 were conducted at HMI. The measurement details are provided in the companion paper (Balasus et al., 2021). Briefly, the water-soluble ionic components of $PM_{2.5}$ were measured with a Particle-into-Liquid Sampler coupled to a dual Ion Chromatograph (PILS-IC, Metrohm) operated according to Valerino et al. (2017). NH_3 was measured with an AiRRmonia Analyzer (RR Mechatronics) (Norman et al., 2009). Meteorological parameters were measured with a Vaisala MAWS201 Met Station at 1-minute resolution.

The 5-minute NH_3 measurements and 1-minute meteorological measurements were averaged to the 20-mintue sampling time of the PILS-IC. Aerosol pH for each 20-min sample was calculated according to the NH_3 partitioning method presented in Zheng et al. (2020). This method uses the relevant temperature-dependent equilibrium constants and the measured concentrations of NH_3 and NH_4^+ to calculate pH. The method of Zheng et al. (2020) is based upon a similar approach in prior studies (Hennigan et al., 2015; Keene et al., 2004); the two methods are identical, with minor differences only due to equilibrium constant values used based on ranges provided in the literature. Indeed, very close agreement was observed (slope = 0.967, R^2 = 0.977, n = 872) in calculated pH between the NH_3 partitioning methods of Zheng et al. (2020) and Hennigan et al. (2015). The aqueous phase NH_4^+ concentration is derived from the mass concentration of NH_4^+ from the PILS-IC and the ALWC. The ISORROPIA-II thermodynamic equilibrium model was used to calculate ALWC using the PILS-IC, NH_3, and meteorological data as inputs (Fountoukis & Nenes, 2007). The model was run in forward mode

(NH_3 and aerosol NH_4^+ were input at total NH_3) using the metastable assumption according to the recommendation of Guo et al. (2015).

Although ISORROPIA can provide pH, the NH_3 partitioning method was used for pH calculations in this study:

$$pH = pK^*_{a,NH_3} + log_{10}\frac{[NH_3(aq)] + [NH_3(g)]}{[NH_4^+(aq)]} \quad (1)$$

$$[NH_3(g)] = \frac{p_{NH_3}\rho_w}{RT\ AWC} \quad (2)$$

$$K^*_{a,NH_3} = \frac{[H^+(aq)]([NH_3(aq)] + [NH_3(g)])}{[NH_4^+(aq)]} = K_{a,NH_3}\left(1 + \frac{\rho_w}{H_{NH_3}RT\ AWC}\right) \quad (3)$$

where in Equation 1, $[NH_3(aq)]$ is the molality of NH_3 in solution (mol kg^{-1}, calculated by multiplying H_{NH_3} and p_{NH_3}), $[NH_3(g)]$ is the equivalent molality of gaseous NH_3 in solution (mol kg^{-1}, given by Equation 2), and $[NH_4^+(aq)]$ is the molality of NH_4^+ in solution (mol kg^{-1}). Equation 2 calculates $[NH_3(g)]$, where p_{NH_3} is the partial pressure of NH_3 (atm), ρ_w is the density of water (μg m^{-3}), R is the gas constant (atm L mol^{-1} K^{-1}), T is temperature (K), and AWC is aerosol water content (μg m^{-3} air). Equation 3 calculates the last unknown term in Equation 1, which is K^*_{a,NH_3}, the effective dissociation constant (where H_{NH_3} is the Henry's law constant of NH_3 in mol kg^{-1} atm^{-1}).

Direct measurements of aerosol pH are not available to test model predictions so the partitioning of semi-volatile species that depend on pH, most commonly NH_3/NH_4^+ and HNO_3/NO_3^-, is a key metric used to evaluate model performance (Pye et al., 2020). ISORROPIA is used extensively for predictions of pH; however, in this study the measured and ISORROPIA-predicted values of NH_3 partitioning ($\varepsilon_{NH3} = NH_3/(NH_3 + NH_4^+)$) did not always agree well (Fig. S2). There were systematic differences in pH between the two methods (mean pH difference = 0.6 pH units), and they were not correlated ($R^2 = 0.097$, not shown). The source

of the discrepancy in NH_3 partitioning (ISORROPIA modeled versus measurement-calculated) is unknown, though it is not likely the result of an incorrect assumption of equilibrium (see the SI and the companion paper Balasus et al. (2021) for more details).

Commonly, a reasonable estimate of measurement errors associated with the species of interest are on the order of 15% + 1 nmol m^{-3} for online sampling methods (Murphy et al., 2017). Utilizing this estimate in the extreme acidic case (ambient observed SO_4^{2-} and NO_3^- adjusted to + 15% + 1 nmol m^{-3}; NH_4^+ adjusted to – 15% – 1 nmol m^{-3}) or non-acidic case (SO_4^{2-} and NO_3^- adjusted down by – 15% – 1 nmol m^{-3} and NH_4^+ adjusted up by + 15% + 1 nmol m^{-3}), the uncertainty of aerosol pH was predicted to vary by 0.1 – 1 pH units (Murphy et al. 2017). Similarly, Pye et al. (2020) reported that in cases for RH above 60%, deviations of the ISORROPIA-predicted pH and the IUPAC-defined pH are less than one pH unit. The present calculations have similar uncertainties in the pH calculations.

3 Results and Discussion

3.1 Meteorological effect on pH

As in many cities, the urban heat island effect in Baltimore evolves throughout the day, with urban-rural temperature and RH gradients peaking at night (Battaglia et al., 2017). Meteorological conditions at HMI demonstrate unique features associated with the land-water transition. At night, the average temperature observed at HMI was close to conditions observed in downtown Baltimore but transitioned to match the conditions at a nearby rural site during the day (Fig. 1a). Overall, the range in average hourly temperatures at HMI was lower (4.3 °C; 22.5 – 26.8 °C) than the averages observed at either the downtown site (range 6.2 °C; 22.8 – 29.0 °C) or the rural site (range 8.8 °C; 17.5 – 26.3 °C). Likewise, the average hourly RH profile at HMI

had a significantly smaller range (13.7%; 61.7 – 75.4%) than the RH profiles at the downtown (range 22.1%; 53.2 – 75.3%) or rural sites (range 30.3%; 55.9 – 86.2%) (Fig. 1b). The differences shown in Fig. 1 were due to the proximity of HMI to the Chesapeake Bay and have several implications for aerosol pH, which will be discussed in detail below.

Due to the meteorological conditions discussed above, the diurnal profile of ALWC at HMI was unique (Fig. 2a). Typical profiles of ALWC in the eastern US closely follow RH, with minima in the afternoon and maxima at night or in the pre-dawn morning hours (Guo et al., 2015; Battaglia et al., 2017). During OWLETS-2, ALWC did not show a distinct diurnal profile that was correlated with RH. Instead, the highest median ALWC at HMI occurred between 12:00 – 14:00, (local time, LT; during the study this is UTC-4) (Fig. 2a). This daily peak in ALWC coincided with a pronounced enhancement in aerosol NO_3^-, which is discussed in the companion paper (Balasus et al., 2021). The partitioning of NH_3, ε_{NH3}, also showed a diurnal profile that was unexpected (Fig. 2b). Due to the strong temperature dependence of vapor pressure and equilibrium constants, NH_3 partitioning typically shifts towards the gas-phase during the daytime (ε_{NH3} increases) and shifts towards the aerosol phase at night (ε_{NH3} decreases) (Guo et al., 2017). The increase in gas-phase NH_3 emissions with increasing temperature can also contribute to an elevated ε_{NH3} during the daytime. The diurnal profile of ε_{NH3} observed at HMI did not follow temperature, as the median ε_{NH3} peaked during the 06:00 – 08:00 LT, and decreased slightly into the afternoon (Fig. 2b). This shows a shift of NH_3 partitioning towards the condensed phase as daily temperatures peaked. This was enabled by the ALWC remaining steady throughout the afternoon. Overall, the median ε_{NH3} value for the entire OWLETS-2 study was 0.915, showing NH_3 partitioning was shifted towards the gas-phase.

The diurnal profile of aerosol pH computed using the NH_3 partitioning method followed a qualitatively similar pattern to prior studies (Battaglia et al. 2017), with maxima in the early morning and minima in the afternoon; however, there was a much smaller amplitude in the median hourly pH values (Fig. 3). The highest median pH value (1.97) was observed between 07:00 – 08:00 LT, while the lowest median pH (1.50) was observed between 16:00 – 17:00 LT. For the entire study, there was only a ~1 pH unit difference between the 10th and 90th percentile values (1.39 and 2.36, respectively). The relatively muted diurnal profile of aerosol pH was due to the unique meteorology that resembled a nearby urban site at night and transitioned to match the nearby rural site during the day. The companion paper shows the diurnal profiles of aerosol inorganic composition (Balasus et al., 2021). Figures 2 and 3 are consistent with recent studies that demonstrate the high sensitivity of pH to meteorological factors (Battaglia et al., 2017; Tao & Murphy, 2019; Zheng et al., 2020). It is interesting to note that the ISORROPIA predictions of aerosol pH yield a distinctly different diurnal profile than the pH predicted by NH_3 partitioning (Fig. S3). The difference in pH between the two methods peaked in the afternoon between 12:00 – 14:00 LT, when particles were most acidic, and was a minimum in the early morning when pH was highest (Fig. S3). The reason for these discrepancies are explored in the discussion below.

Results suggest that pH was most sensitive to temperature changes at HMI during OWLETS-2 (Fig. 4a). Across the full temperature range, the observed pH sensitivity to temperature was -0.047 K^{-1}. A recent study contrasting pH in the southeast US and the North China Plain found that temperature affects pH linearly at a rate of approximately -0.055 K^{-1} (Zheng et al., 2020). A separate study from a Canadian observational network found that the pH-temperature dependence is not linear, but changes with temperature (Tao and Murphy, 2019;

Tao, 2020). Over the range of conditions observed during OWLETS-2, Tao (2020) computed a pH sensitivity to temperature of approximately -0.045 K^{-1} to -0.055 K^{-1}. In a previous study, the pH sensitivity to temperature in Baltimore was -0.048 K^{-1}, though this was calculated for conditions of constant atmospheric composition (Battaglia et al., 2017). While the present results share consistencies with these studies, the results in Fig. 4a suggest important differences, as well. An increase in pH was observed with increasing temperature for conditions below 293 K (n=156). In the companion paper, NH_3 concentrations dramatically increased with temperature < 293 K but exhibited a much weaker dependence on temperature for conditions > 293 K (Balasus et al., 2021). Under the warmer conditions, the pH relationship with temperature was linear during OWLETS-2, with a sensitivity of -0.085 K^{-1} (Fig. 4a). The results in Fig. 4a are consistent with Tao (2020), as they demonstrate the offsetting responses of pH to temperature through effects on NH_3 emissions and partitioning.

These results contribute to the growing body of work demonstrating the importance of temperature to aerosol pH. Collectively, these studies suggest that the sensitivity of pH to temperature is constrained between -0.045 K^{-1} and -0.085 K^{-1}, although the present results illustrate circumstances where a positive relationship between temperature and pH can exist, as well. It is notable that similar $\Delta pH/\Delta T$ values are observed across a range of locations and for variable data sets that include monthly averages of long-term observations (Tao and Murphy, 2019) and 20-min measurements made over a period of weeks (presented here).

Aerosol pH was not strongly affected by ALWC over the range of conditions observed during OWLETS-2, except at ALWC below 1 μg m^{-3} (Fig. 4b). At the lowest ALWC levels, the increase in pH occurs because of the diluting effect of water, however, at ALWC above 1 μg m^{-3}, other factors appear to be more important (e.g., temperature). ALWC was recently identified as

the most significant contributor to regional pH differences (Zheng et al., 2020). In that study, the pH-ALWC relationship was highly non-linear, with the greatest sensitivity calculated at ALWC at levels < 25 μg m^{-3}, conditions corresponding to all the OWLETS-2 observations. Tao (2020) found that pH is extremely sensitive to RH, presumed to be a surrogate for ALWC, when RH was < 20% or RH > 80%; however, pH was quite insensitive to RH variations in the region of 20% < RH < 80%. Approximately 25% (208 out of 875) of RH values during OWLETS-2 were above 80%, yet no increase in pH was observed at the highest ALWC, suggesting that other factors were offsetting the diluting effect of water as ALWC increased. It is interesting to note that ISORROPIA predicts a stronger effect of ALWC on pH, with the diluting effect apparent as pH increases with increasing ALWC. A combination of particle mass loading, aerosol composition, and ambient RH are responsible for the variations in ALWC.

The result shown in Fig. 4b is somewhat surprising because NH_3 partitioning was quite sensitive to ALWC (Fig. 5); the relatively invariant aerosol pH is unexpected given the increase in NH_3 uptake in the presence of ALWC. With increasing NH_3 uptake in the presence of, and concurrent with, the increased ALWC, it would be anticipated that aerosol pH would become more basic both through the reaction of NH_3 to form NH_4^+ and due to the dilution effect of liquid water. However, the results of Figures 4 and 5 reveal that despite both the increase in NH_3 uptake and increase in ALWC, aerosol pH remains relatively unchanged, with only a 0.5 pH unit change at the highest values of ALWC. NH_3 partitioning shifted towards the condensed phase (ε_{NH3} decreased) at increasing ALWC, consistent with the results of Nenes et al. (2020). ε_{NH3} was more sensitive to ALWC than it was to either temp or RH (Fig. S5). This result shows the importance that ALWC can have on $PM_{2.5}$ mass concentrations, as water serves as an important medium enhancing the condensation of organic and inorganic water-soluble species (Carlton et

al., 2018; El-Sayed et al., 2016). Fig. 5 demonstrates the importance of ALWC in changing the dry deposition of reactive nitrogen species. Nenes et al. (2021) predicts that NH_3 and HNO_3 dry deposition rates will both be high under the conditions observed during OWLETS-2 (i.e., ALWC < 10 μg m^{-3} and pH ~ 1.5). This is also consistent with a modeling study showing increased dry deposition of reactive nitrogen in coastal regions, including the OWLETS-2 study domain (Loughner et al., 2016).

3.2 Composition Effects on Aerosol pH

In contrast to meteorological factors, aerosol composition did not have a major effect on pH variability during OWLETS-2. Consistent with prior studies, neither the sulfate concentration nor the NH_4^+:SO_4^{2-} molar ratio contributed significantly to pH variability (Weber et al., 2016; Hennigan et al., 2015). Fig. 4c shows that pH was also relatively insensitive to the Tot-NH_3 concentration, in agreement with the results from other locations (Zheng et al., 2020; Tao, 2020; Weber et al., 2016). While the predictions of ISORROPIA generally did not capture the trends between pH and the meteorological factors, it is interesting to note that ISORROPIA predicts that pH is relatively insensitive to Tot-NH_3, as well, except at the highest concentrations (Fig. S4).

Composition and concentration differences between HMI and the urban and rural sites are analyzed in more detail in the companion paper (Balasus et al., 2021). In the companion paper, episodic NH_3 events that derived from dairy, poultry, and industrial sources were characterized (Balasus et al., 2021). For the events with complete aerosol composition and meteorology data (8 out of 11 NH_3 events total), mean and medial aerosol pH (2.00 and 1.96, respectively) were only moderately higher than the study mean and median pH values (1.85 and

1.83, respectively); this difference is not statistically significant at the 95% confidence interval. This includes an aerosol pH of 1.92 at the peak NH_3 concentration observed during the entire study (19.3 μg m^{-3}), an event influenced by industrial emissions near downtown Baltimore (Balasus et al., 2021). Together, the results suggest that pH may be more affected by the proximity of the HMI site to the Chesapeake Bay than it was to regional agricultural NH_3 emissions, or to episodic NH_3 events from local industrial sources.

3.3 Case Study: Effect of NVCs on pH

NVCs affect thermodynamic predictions of NH_3 partitioning and thus, pH (Guo et al., 2018; Vasilakos et al., 2018). Seawater is alkaline and primary marine emissions contain high concentrations of NVCs (O'Dowd & De Leeuw, 2007). Marine aerosols rapidly acidify, typically in seconds or minutes, though the timescale depends upon particle size (Angle et al., 2021; Pszenny et al., 2004). Studies have examined the acidity of sea spray aerosols and their evolution but none, to our knowledge, have done so in a polluted urban environment. The OWLETS-2 study offered a unique opportunity to analyze the pH of primary marine particles emitted within several km of a large urban area. The Chesapeake Bay is brackish, with increasing salinity moving down the bay towards the Atlantic Ocean (Pritchard, 1952). Near the OWLETS-2 measurement site at HMI, salinity is variable but average conditions are ~5 g kg^{-1} (www.chesapeakebay.net, last accessed 20-November 2020). This is about a factor of seven lower than typical seawater, but shows the potential for primary emissions to contribute salts that could impact aerosol pH at HMI.

Elevated concentrations of Na^+ and Cl^- in $PM_{2.5}$ were infrequently observed during OWLETS-2, with one notable 36-hour period showing evidence of primary marine impact. Na^+

and Cl^- were well-correlated (R^2 = 0.78) from 11-June to 13-June, a period that coincided with the highest concentrations of both species (Fig. 6 and Fig. 7). It is noteworthy that wind speeds were not elevated during this time (average winds = 3.1 m s^{-1} compared to campaign-average wind speeds of 2.9 m s^{-1}); longer-term measurements would be needed to characterize factors driving the primary bay emissions. During this event, the pH calculation using NH_3 partitioning suggests that the primary marine emissions had a minimal effect on aerosol pH. The average pH during this period was 1.98, which was only slightly higher than the average for the entire study (1.85). Further, as the total Na^+ + Cl^- concentration increased by more than an order of magnitude, from 0.05 μg m^{-3} around 18:00 LT on 11 June to 0.9 μg m^{-3} at 09:00 LT on 12 June, the pH only increased by 0.1 pH unit during the same period (Fig. 6). Gas-phase NH_3 data were not available for the entire NaCl event, so pH calculations were limited to the first ~20 hours.

The pH predictions from ISORROPIA during this period display a more significant effect on aerosol pH. The average pH predicted by ISORROPIA is 3.08, which is 0.7 pH units higher than the study average from ISORROPIA. Further, while the pH calculated using NH_3 partitioning is insensitive to Na^+ and Cl^-, ISORROPIA predicts a rise of 1.4 pH units as Na^+ and Cl^- increase (Figure 6). The NH_3 partitioning predicted by ISORROPIA deviates from the observations during this event (r = -0.19, Fig. S6). The most likely explanation for this behavior is different chemical compositions of the coarse- and fine-mode particles. Fresh marine emissions acidify quickly, and evidence was found for chemical processing of NaCl. HNO_3 displacement of HCl is a well-known phenomenon in sea salt particles (Brimblecombe & Clegg, 1988). Cl^-:Na^+ ratios slightly above unity were observed when aerosol nitrate concentrations were low, and below unity when nitrate concentrations were elevated (Fig. 7). Nitrate formation, including HNO_3 uptake to sea salt, is highly sensitive to pH (Kakavas et al., 2021; Vasilakos et

al., 2018). Nitrate (along with Na^+ and Cl^-) are direct inputs to ISORROPIA, suggesting that the pH trend in Fig. 6 is due to the increased influence of coarse-mode particles. The PILS inlet was equipped with a 2.5 µm cut-point cyclone (URG-2000-30-EH, URG Corp.), which allows some penetration of particles with d_p < 4.5 µm (http://www.urgcorp.com/products/inlets/teflon-coated-aluminum-cyclones/urg-2000-30eh, last accessed 29 January 2021). Likewise, primary sea salt emissions often exhibit a size distribution tail that extends below 2.5 µm (Feng et al., 2017).

The above analysis identifies limitations computing aerosol pH with both approaches and highlights opportunities to use complementary information from each to inform factors driving aerosol pH. ISORROPIA's assumption of an internally mixed aerosol distribution cannot be applied to predict pH in this system (Fountoukis and Nenes, 2007). However, it does provide insight into the likely presence of coarse mode particles with pH significantly higher than the fine mode. Conversely, Na^+, Cl^- and NO_3^- are not direct inputs into the pH calculation using NH_3 partitioning, though they are used to compute aerosol liquid water, which is an input in the pH calculation (Zheng et al., 2020). These NVCs have been shown to have sometimes significant effects on the ratios of ammonium-to-sulfate, which could lead to inconsistencies in the calculation of aerosol pH when considered in the ALWC calculation only (Guo et al. 2015). NH_4^+ resides predominantly in the fine mode (Seinfeld & Pandis, 2016), so the partitioning approach is unlikely to capture the acidity of the coarse mode or fine-mode particles in the tail of the distribution of primary emissions that may be externally mixed with secondary particles, such as dust or sea salt. This may lead to underestimates of NVC effects on aerosol pH using the partitioning approach. The combined information from both methods suggests that aerosols sampled at HMI during the NaCl event were characterized by a strong size-dependent pH gradient, with fine-mode particles more acidic (pH ~2) than the coarse mode (pH up to 4.5).

Estimates of pH derived from size-segregated aerosol composition measurements have observed the same phenomenon (Angle et al., 2021; Fang et al., 2017; Kakavas et al., 2021; Keene et al., 2002).

4 Conclusions

There is growing recognition of the importance of aerosol pH affecting atmospheric processes relevant to public health and ecosystems (Fang et al., 2017; Nenes et al., 2021). Observations of spatial and temporal variations in pH are needed so that the factors that control pH and contribute to variability in different environments can be fully understood. This study is unique as it represents the first characterization of aerosol pH at a land-water transition site near a large urban area. Baltimore, MD, is impacted by regional agricultural emissions and by industrial point-source emissions of NH_3. The companion paper examines the sources of episodic NH_3 events and the associated effects on aerosol composition (Balasus et al., 2021). Although average and peak NH_3 concentrations during this study were significantly higher than a nearby inland site, the effects on aerosol pH appear relatively insignificant, as pH during the peak events was only ~0.1 pH unit higher than non-event periods. This finding is consistent with studies at other locations that show aerosol pH is often insensitive to Tot-NH_3 and to the aerosol NH_4:SO_4 ratio (Weber et al., 2016; Zheng et al., 2020; Tao and Murphy, 2019).

The unique characteristics of the OWLETS-2 study and measurement locations also offered insight into the composition and meteorological influences on aerosol pH. In the companion paper, the composition effects were shown to be muted in comparison to the meteorological effects (Balasus et al., 2021). It was shown that the unique diurnal profiles, particularly in ALWC (which did not correlate with RH) and ε_{NH3} (which did not correlate with

T) resulted in meteorological factors, notably temperature, having the most important influence on aerosol pH. Across the full temperature range of the study, the observed pH sensitivity to temperature was -0.047 K^{-1}, with increases in sensitivity up to -0.085 K^{-1} when the temperature was > 293 K. The sensitivity of aerosol pH shown here is in good agreement with previous studies in the Baltimore region and beyond, *e.g.* Toronto (Tao and Murphy, 2019; Battaglia et al. 2017). Conversely, aerosol pH was not strongly affected by ALWC during the OWLETS-2 study, except when ALWC was below 1 μg m^{-3}, in contrast to the results of Zheng et al. (2020). These results of Zheng et al. (2020) in identifying ALWC as the most important factor driving aerosol pH variability were derived from the results of studies in multiple locations, including bulk aqueous solutions. However, this analysis suggests that the factors that drive aerosol pH variability may exhibit important site-to-site differences that must be considered before generalizations are applied.

A case study of the NVC effect on aerosol pH had significantly different outcomes depending on the method for calculating pH. ISORROPIA predicted a pH increase of ~ 1.4 pH units during an event with primary aerosol emissions from the Chesapeake Bay, while the pH calculation using NH_3 partitioning predicted a much less significant effect (~0.1 pH unit). This difference is attributed to the likely presence of externally mixed particles during the events, which may include primary marine emissions elevated in NVCs. Bougiatioti et al. (2016) evaluated aerosol pH at a remote site in the Mediterranean, where samples with a marine origin demonstrated vastly different pH between fine (avg. pH = 0.4) and coarse mode (average pH = 7.3) particles. Similarly, Keene et al. (2002) demonstrated the effect of marine aerosol size distribution on aerosol pH, with fine mode particles predicted to reside in the range of 1-2, with super-μm particles to reside in the range of 3-4, consistent with the current results. Hence, a

limitation of this study is the lack of size-resolved aerosol composition measurements. This study underscores the need to evaluate assumptions of internally mixed aerosols when applying pH calculations, which may be a critical factor in overestimating the effects of NVCs on pH. Models with size-resolved aerosol composition may be required to capture this effect across scales in future studies (Kakavas et al., 2021).

Data Availability

Data are available at https://www-air.larc.nasa.gov/cgi-bin/ArcView/owlets.2018.

Supplement

Supplemental Information is available for this article at:

Acknowledgements

Annmarie G. Carlton and Christopher J. Hennigan acknowledge funding from the National Science Foundation, AGS-1719252 and AGS-1719245. Ruben Delgado and Vanessa Caicedo acknowledge support by the Maryland Department of the Environment (contract no. U00P8400651). Nicholas Balasus and Katherine Ball received support through the NOAA Office of Education, Educational Partnership Program with Minority Serving Institutions (EPP/MSI) and the Cooperative Science Center for Earth System Sciences and Remote Sensing Technologies (grant no. NA16SEC4810008).

Author Contributions

CH, AC, and RD conceived the analysis and study participation. MB, NB, and KB collected and analyzed the PILS-IC and NH_3 data. NB, MB, and CH conducted the thermodynamic modeling analyses. VC and AC provided analytical input and interpretation. NB, CH, KB, and MB wrote the manuscript. All authors provided feedback and revisions to the manuscript.

Competing Interests

The authors declare they have no conflict of interest.

Figures

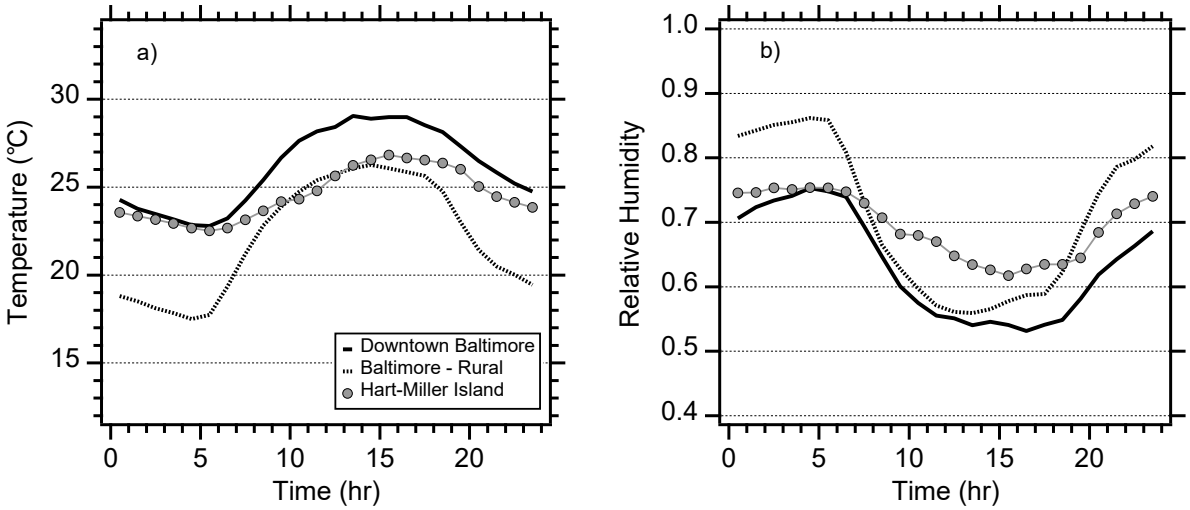


Figure 1: Diurnal profiles of (a) temperature and (b) relative humidity at three sites during the OWLETS-2 study. Hart-Miller Island (HMI) is a land-water transition site and was the location of aerosol composition and gas-phase measurements during the campaign. Temperatures at HMI resembled the downtown location during the night but showed characteristics of the rural site during the day. RH at HMI was between the urban and rural sites at night but was elevated during the daytime due to the Chesapeake Bay.

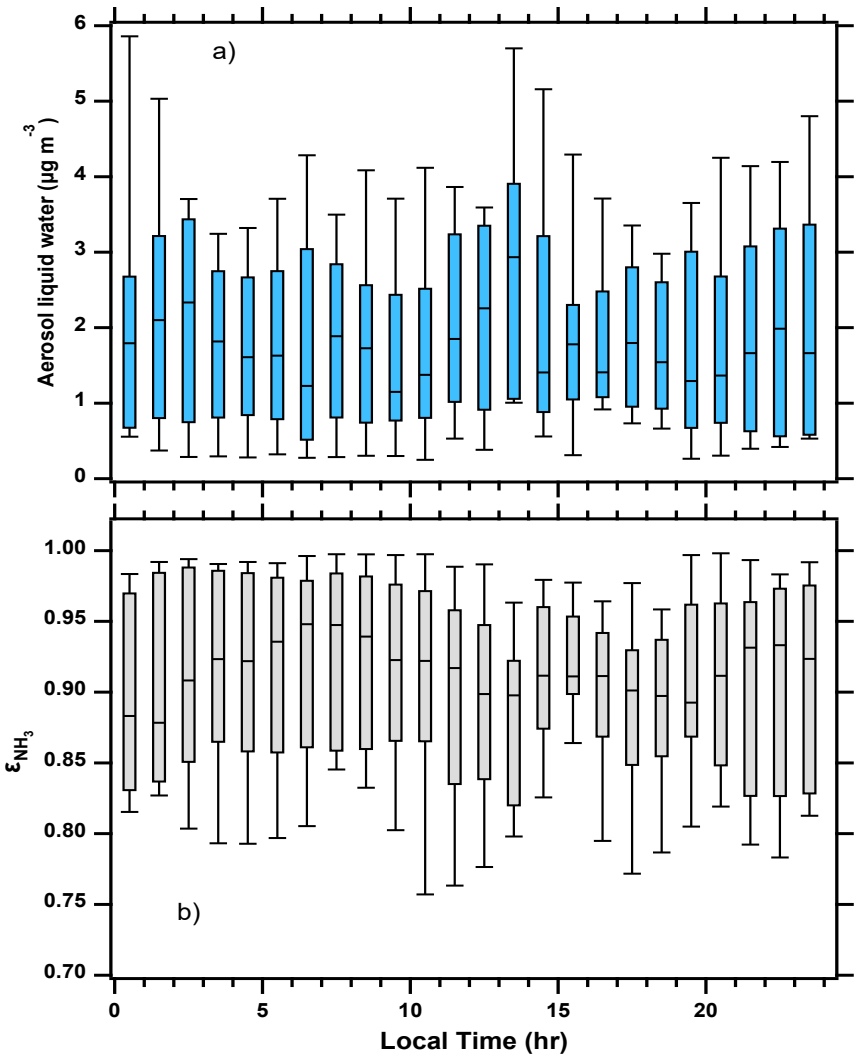


Figure 2: Box plots of (a) aerosol liquid water and (b) ε_{NH3} (ε_{NH3} = $NH_3(g)/(NH_3(g) + NH_4^+(aq))$) during the OWLETS-2 study. The statistics shown are the median, quartiles, 10th and 90th percentiles.

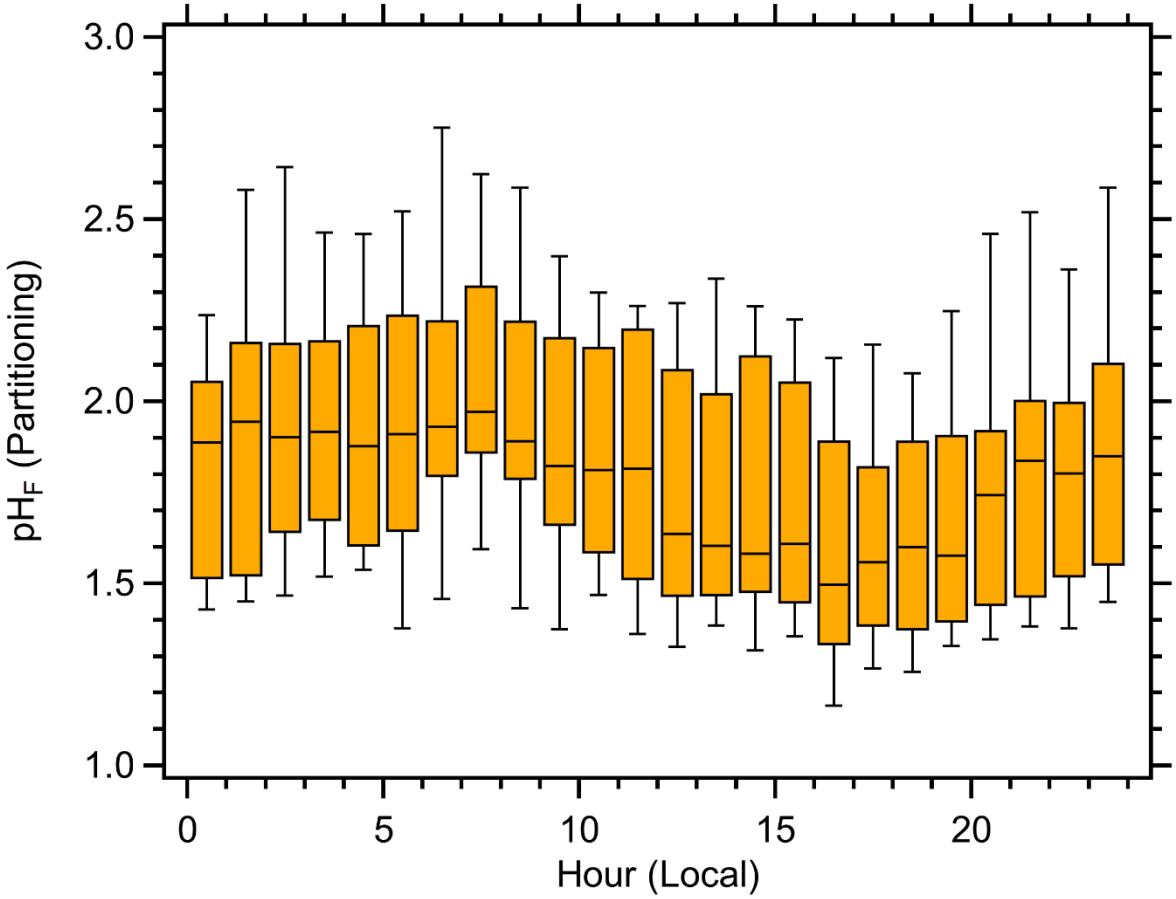
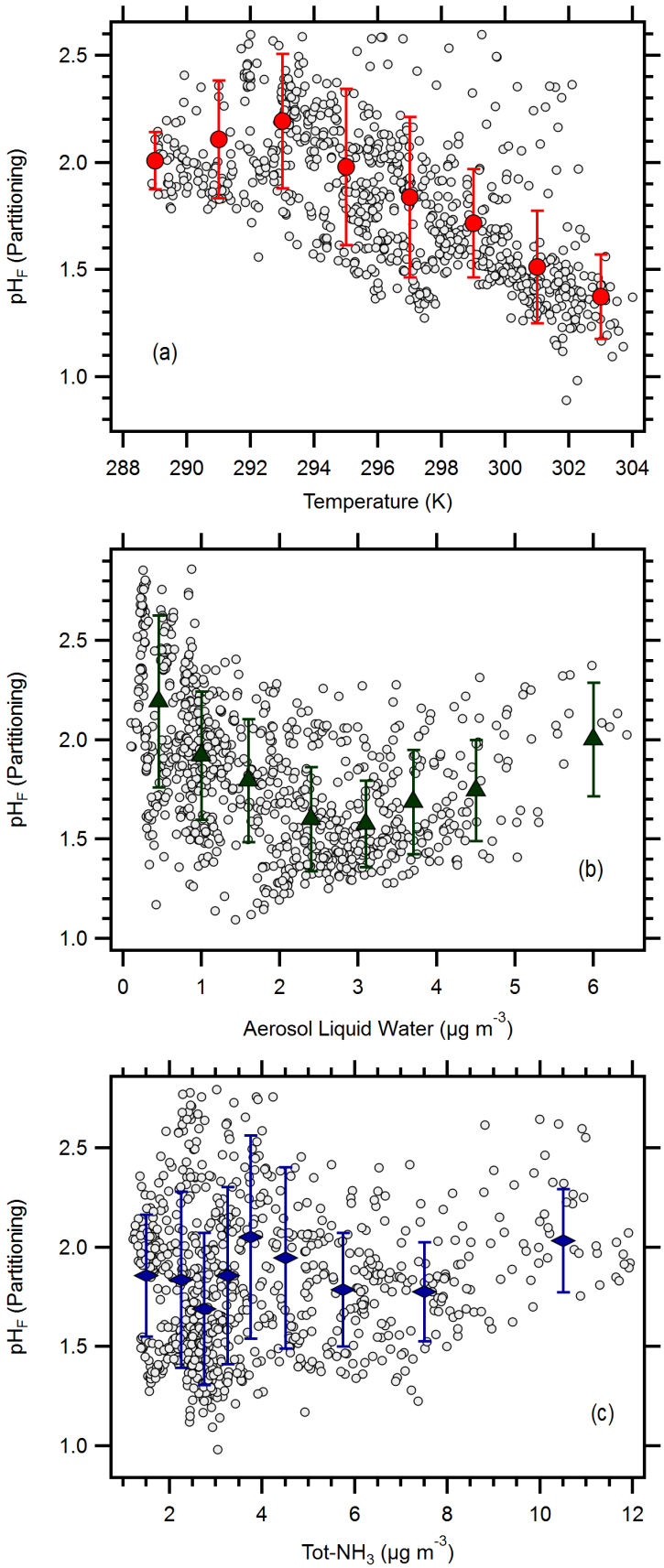


Figure 3: Box plot of the aerosol pH diurnal profile calculated using the NH_3 partitioning method of at Hart-Miller Island during OWLETS-2. The statistics shown are the median, quartiles, 10th and 90th percentiles.


pH$_F$ (Partitioning)
Temperature (K)
(a)
Aerosol Liquid Water (μg m^{-3})
(b)
Tot-NH$_3$ (μg m^{-3})
(c)

439

Figure 4: Relationship between aerosol pH and (a) temperature, (b) aerosol liquid water, and (c) total NH_3 (Tot-NH_3 = NH_3 + NH_4^+). Symbols represent mean values while error bars represent standard deviations; bins were limited to a maximum of 160 points per bin.

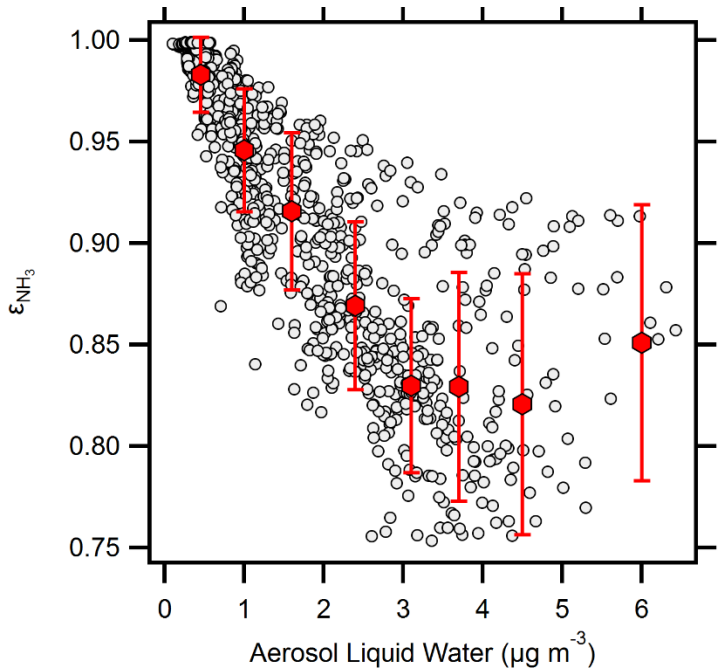


Figure 5: Relationship between NH_3 partitioning ($\varepsilon_{NH3} = NH_3/(NH_3 + NH_4^+)$) and aerosol liquid water. Symbols represent mean values while error bars represent standard deviations; bins were limited to a maximum of 160 points per bin.

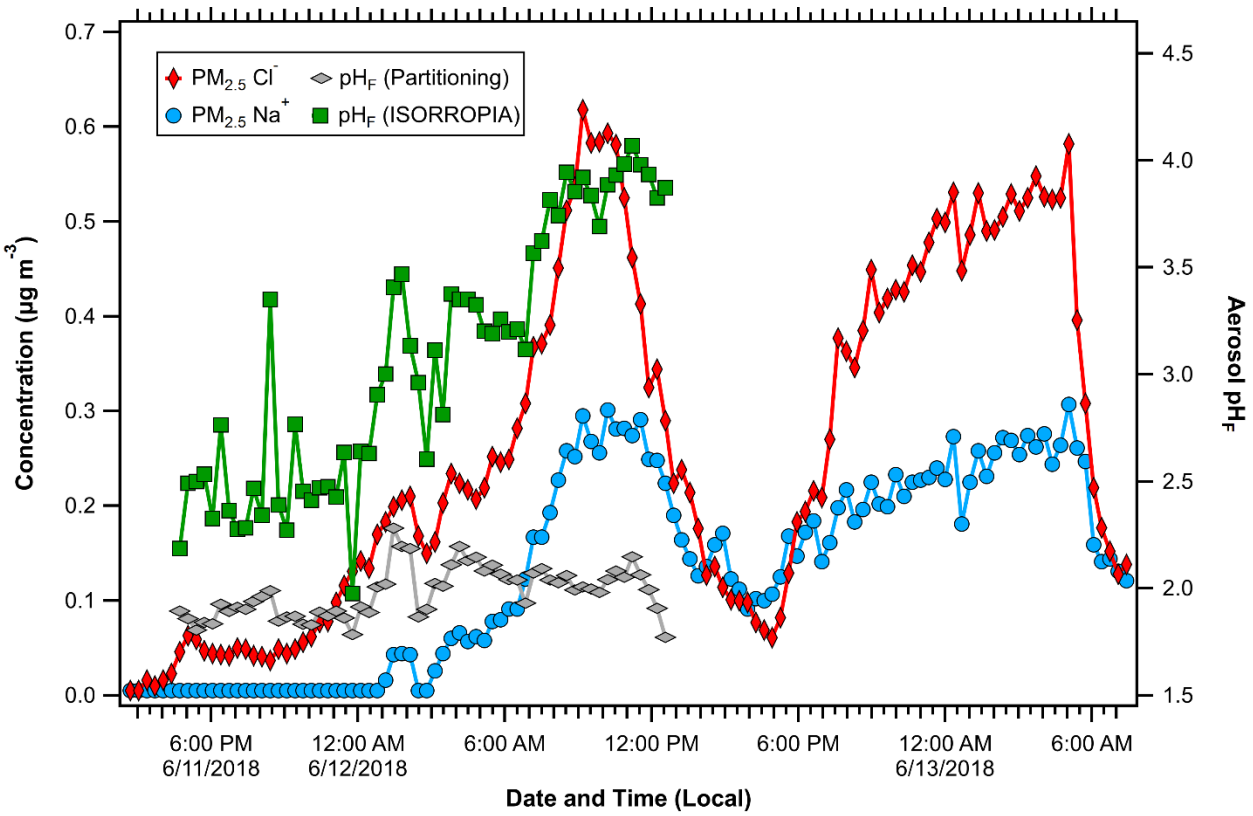


Figure 6: Concentrations of $PM_{2.5}$ Na^+ and Cl^- during a period with primary Chesapeake Bay emissions. Aerosol pH calculated by NH_3 partitioning and ISORROPIA show different behaviors, suggesting the aerosol distribution was externally mixed during this time.

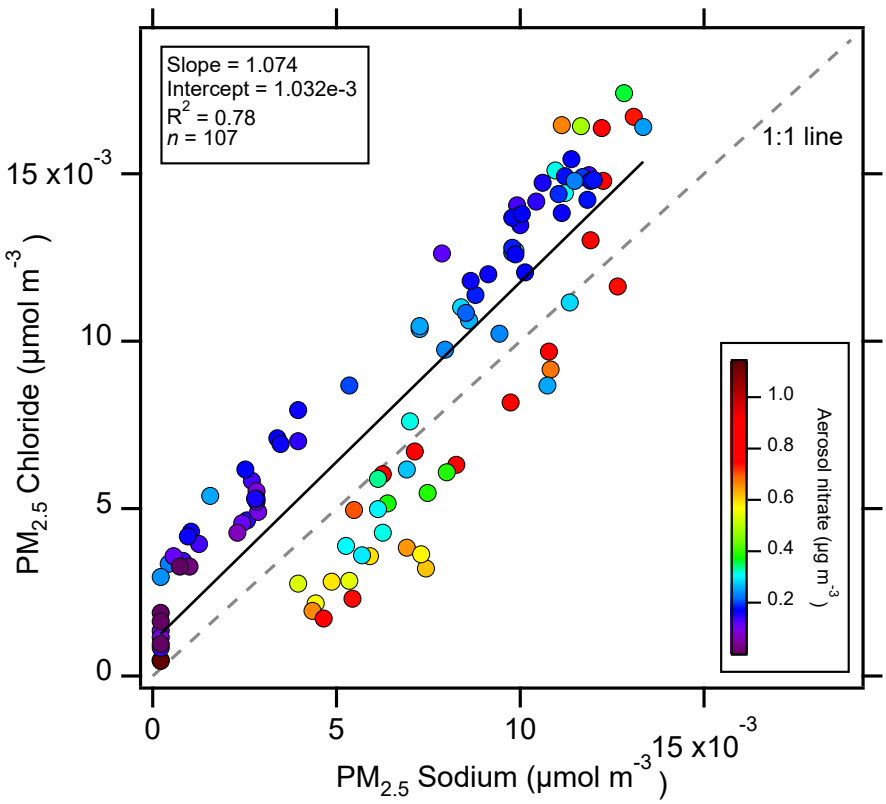


Figure 7: Correlation between $PM_{2.5}$ Na^+ and Cl^- during the event shown in Figure 6. Lower Cl^-:Na^+ ratios were observed at higher NO_3^- concentrations, suggesting HNO_3 uptake displaced HCl.

References

Angle, K. J., Crocker, D. R., Simpson, R. M. C., Mayer, K. J., Garofalo, L. A., Moore, A. N., Garcia, S. L. M., Or, V. W., Srinivasan, S., Farhan, M., Sauer, J. S., Lee, C., Pothier, M. A., Farmer, D. K., Martz, T. R., Bertram, T. H., Cappa, C. D., Prather, K. A., & Grassian, V. H. (2021). Acidity across the interface from the ocean surface to sea spray aerosol. *Proceedings of the National Academy of Sciences of the United States of America*, *118*(2), Article e2018397118. https://doi.org/10.1073/pnas.2018397118

Balasus, N., Battaglia Jr, M. A., Ball, K., Caicedo, V., Delgado, R., Carlton, A. G., & Hennigan, C. J. (2021). Urban aerosol chemistry at a land–water transition site during summer – Part 1: Impact of agricultural and industrial ammonia emissions. *Atmos. Chem. Phys.*, *21*(17), 13051-13065. https://doi.org/10.5194/acp-21-13051-2021

Battaglia Jr, M. A., Weber, R. J., Nenes, A., & Hennigan, C. J. (2019). Effects of water-soluble organic carbon on aerosol pH. *Atmos. Chem. Phys.*, *19*(23), 14607-14620. https://doi.org/10.5194/acp-19-14607-2019

Battaglia, M. A., Douglas, S., & Hennigan, C. J. (2017). Effect of the Urban Heat Island on Aerosol pH. *Environ. Sci. Technol.*, *51*(22), 13095-13103. https://doi.org/10.1021/acs.est.7b02786

Bougiatioti, A., Nikolaou, P., Stavroulas, I., Kouvarakis, G., Weber, R., Nenes, A., Kanakidou, M., & Mihalopoulos, N. (2016). Particle water and pH in the eastern Mediterranean: source variability and implications for nutrient availability. *Atmos. Chem. Phys.*, *16*(7), 4579-4591. https://doi.org/10.5194/acp-16-4579-2016

Boyer, H. C., Gorkowski, K., & Sullivan, R. C. (2020). In Situ pH Measurements of Individual Levitated Microdroplets Using Aerosol Optical Tweezers. *Analytical Chemistry*, *92*(1), 1089-1096. https://doi.org/10.1021/acs.analchem.9b04152

Brimblecombe, P., & Clegg, S. L. (1988). The Solubility and Behavior of Acid Gases in the Marine Aerosol. *Journal of Atmospheric Chemistry*, *7*(1), 1-18. https://doi.org/10.1007/bf00048251

Carlton, A. M. G., Pye, H. O. T., Baker, K. R., & Hennigan, C. J. (2018). Additional benefits of federal air quality rules: model estimates of controllable biogenic secondary organic aerosol. *Environmental Science & Technology*. https://doi.org/10.1021/acs.est.8b01869

Craig, R. L., Peterson, P. K., Nandy, L., Lei, Z., Hossain, M. A., Camarena, S., Dodson, R. A., Cook, R. D., Dutcher, C. S., & Ault, A. P. (2018). Direct Determination of Aerosol pH: Size-Resolved Measurements of Submicrometer and Supermicrometer Aqueous Particles. *Analytical Chemistry*, *90*(19), 11232-11239. https://doi.org/10.1021/acs.analchem.8b00586

El-Sayed, M. M. H., Amenumey, D., & Hennigan, C. J. (2016). Drying-Induced Evaporation of Secondary Organic Aerosol during Summer. *Environmental Science & Technology*, *50*(7), 3626-3633. https://doi.org/10.1021/acs.est.5b06002

Fang, T., Guo, H. Y., Zeng, L. H., Verma, V., Nenes, A., & Weber, R. J. (2017). Highly Acidic Ambient Particles, Soluble Metals, and Oxidative Potential: A Link between Sulfate and Aerosol Toxicity. *Environmental Science & Technology*, *51*(5), 2611-2620. https://doi.org/10.1021/acs.est.6b06151

Feng, L., Shen, H., Zhu, Y., Gao, H., & Yao, X. (2017). Insight into Generation and Evolution of Sea-Salt Aerosols from Field Measurements in Diversified Marine and Coastal Atmospheres. *Scientific Reports*, *7*, Article 41260. https://doi.org/10.1038/srep41260

Fountoukis, C., & Nenes, A. (2007). ISORROPIA II: a computationally efficient thermodynamic equilibrium model for K^+-Ca^{2+}-Mg^{2+}-NH_4^+-Na^+-SO_4^{2-}-NO_3^--Cl^--H_2O aerosols. *Atmos. Chem. Phys.*, *7*(17), 4639-4659. https://doi.org/10.5194/acp-7-4639-2007

Guo, H., Liu, J., Froyd, K. D., Roberts, J. M., Veres, P. R., Hayes, P. L., Jimenez, J. L., Nenes, A., & Weber, R. J. (2017). Fine particle pH and gas–particle phase partitioning of inorganic species in Pasadena, California, during the 2010 CalNex campaign. *Atmos. Chem. Phys.*, *17*(9), 5703-5719. https://doi.org/10.5194/acp-17-5703-2017

Guo, H., Nenes, A., & Weber, R. J. (2018). The underappreciated role of nonvolatile cations in aerosol ammonium-sulfate molar ratios. *Atmos. Chem. Phys.*, *18*(23), 17307-17323. https://doi.org/10.5194/acp-18-17307-2018

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., & Weber, R. J. (2015). Fine-particle water and pH in the southeastern United States. *Atmos. Chem. Phys.*, *15*(9), 5211-5228. https://doi.org/10.5194/acp-15-5211-2015

He, H., Stehr, J. W., Hains, J. C., Krask, D. J., Doddridge, B. G., Vinnikov, K. Y., Canty, T. P., Hosley, K. M., Salawitch, R. J., Worden, H. M., & Dickerson, R. R. (2013). Trends in emissions and concentrations of air pollutants in the lower troposphere in the Baltimore/Washington airshed from 1997 to 2011. *Atmospheric Chemistry and Physics*, *13*(15), 7859-7874. https://doi.org/10.5194/acp-13-7859-2013

Hennigan, C. J., Izumi, J., Sullivan, A. P., Weber, R. J., & Nenes, A. (2015). A critical evaluation of proxy methods used to estimate the acidity of atmospheric particles. *Atmos. Chem. Phys.*, *15*(5), 2775-2790. https://doi.org/10.5194/acp-15-2775-2015

Jang, M., Sun, S., Winslow, R., Han, S., & Yu, Z. (2020). In situ aerosol acidity measurements using a UV–Visible micro-spectrometer and its application to the ambient air. *Aerosol Science and Technology*, *54*(4), 446-461. https://doi.org/10.1080/02786826.2020.1711510

Kakavas, S., Patoulias, D., Zakoura, M., Nenes, A., & Pandis, S. N. (2021). Size-resolved aerosol pH over Europe during summer. *Atmos. Chem. Phys.*, *21*(2), 799-811. https://doi.org/10.5194/acp-21-799-2021

Kanakidou, M., Myriokefalitakis, S., Daskalakis, N., Fanourgakis, G., Nenes, A., Baker, A. R., Tsigaridis, K., & Mihalopoulos, N. (2016). Past, Present, and Future Atmospheric Nitrogen Deposition. *J. Atmos. Sci.*, *73*(5), 2039-2047. https://doi.org/10.1175/jas-d-15-0278.1

Keene, W. C., Pszenny, A. A. P., Maben, J. R., & Sander, R. (2002). Variation of marine aerosol acidity with particle size. *Geophysical Research Letters*, *29*(7), Article 1101. https://doi.org/10.1029/2001gl013881

Keene, W. C., Pszenny, A. A. P., Maben, J. R., Stevenson, E., & Wall, A. (2004). Closure evaluation of size-resolved aerosol pH in the New England coastal atmosphere during summer. *J. Geophys. Res.-Atmos.*, *109*(D23), D23307, Article D23307. https://doi.org/10.1029/2004jd004801

Loughner, C. P., Tzortziou, M., Follette-Cook, M., Pickering, K. E., Goldberg, D., Satam, C., Weinheimer, A., Crawford, J. H., Knapp, D. J., Montzka, D. D., Diskin, G. S., & Dickerson, R. R. (2014). Impact of Bay-Breeze Circulations on Surface Air Quality and Boundary Layer Export. *Journal of Applied Meteorology and Climatology*, *53*(7), 1697-1713. https://doi.org/10.1175/jamc-d-13-0323.1

Loughner, C. P., Tzortziou, M., Shroder, S., & Pickering, K. E. (2016). Enhanced dry deposition of nitrogen pollution near coastlines: A case study covering the Chesapeake Bay estuary and Atlantic Ocean coastline. *Journal of Geophysical Research-Atmospheres*, *121*(23), 14221-14238. https://doi.org/10.1002/2016jd025571

Murphy, J. G., Gregoire, P., Tevlin, A., Wentworth, G., Ellis, R., Markovic, M., & VandenBoer, T. (2017). Observational constraints on particle acidity using measurements and modelling of particles and gases [10.1039/C7FD00086C]. *Faraday Discussions*. https://doi.org/10.1039/C7FD00086C

Nenes, A., Pandis, S. N., Kanakidou, M., Russell, A. G., Song, S., Vasilakos, P., & Weber, R. J. (2021). Aerosol acidity and liquid water content regulate the dry deposition of inorganic reactive nitrogen. *Atmos. Chem. Phys.*, *21*(8), 6023-6033. https://doi.org/10.5194/acp-21-6023-2021

Nenes, A., Pandis, S. N., Weber, R. J., & Russell, A. (2020). Aerosol pH and liquid water content determine when particulate matter is sensitive to ammonia and nitrate availability. *Atmos. Chem. Phys.*, *20*(5), 3249-3258. https://doi.org/10.5194/acp-20-3249-2020

Norman, M., Spirig, C., Wolff, V., Trebs, I., Flechard, C., Wisthaler, A., Schnitzhofer, R., Hansel, A., & Neftel, A. (2009). Intercomparison of ammonia measurement techniques at an intensively managed grassland site (Oensingen, Switzerland). *Atmospheric Chemistry and Physics*, *9*(8), 2635-2645. <Go to ISI>://WOS:000265743100002

O'Dowd, C. D., & De Leeuw, G. (2007). Marine aerosol production: a review of the current knowledge. *Philosophical Transactions of the Royal Society a-Mathematical Physical and Engineering Sciences*, *365*(1856), 1753-1774. https://doi.org/10.1098/rsta.2007.2043

Phillips, S. M., Bellcross, A. D., & Smith, G. D. (2017). Light Absorption by Brown Carbon in the Southeastern United States is pH-dependent. *Environmental Science & Technology*. https://doi.org/10.1021/acs.est.7b01116

Pinder, R. W., Adams, P. J., Pandis, S. N., & Gilliland, A. B. (2006). Temporally resolved ammonia emission inventories: Current estimates, evaluation tools, and measurement needs. *Journal of Geophysical Research-Atmospheres*, *111*(D16), Article D16310. https://doi.org/10.1029/2005jd006603

Pritchard, D. W. (1952). Salinity Distribution and Circulation in the Chesapeake Bay Estuarine System. *Journal of Marine Research*, *11*(2), 106-123. <Go to ISI>://WOS:A1952XR64900002

Pszenny, A. A. P., Moldanov, J., Keene, W. C., Sander, R., Maben, J. R., Martinez, M., Crutzen, P. J., Perner, D., & Prinn, R. G. (2004). Halogen cycling and aerosol pH in the Hawaiian marine boundary layer. *Atmospheric Chemistry and Physics*, *4*, 147-168. https://doi.org/10.5194/acp-4-147-2004

Pye, H. O. T., Nenes, A., Alexander, B., Ault, A. P., Barth, M. C., Clegg, S. L., Collett Jr, J. L., Fahey, K. M., Hennigan, C. J., Herrmann, H., Kanakidou, M., Kelly, J. T., Ku, I. T., McNeill, V. F., Riemer, N., Schaefer, T., Shi, G., Tilgner, A., Walker, J. T., Wang, T., Weber, R., Xing, J., Zaveri, R. A., & Zuend, A. (2020). The acidity of atmospheric particles and clouds. *Atmos. Chem. Phys.*, *20*(8), 4809-4888. https://doi.org/10.5194/acp-20-4809-2020

Pye, H. O. T., Zuend, A., Fry, J. L., Isaacman-VanWertz, G., Capps, S. L., Appel, K. W., Foroutan, H., Xu, L., Ng, N. L., & Goldstein, A. H. (2018). Coupling of organic and inorganic aerosol systems and the effect on gas–particle partitioning in the southeastern US. *Atmos. Chem. Phys.*, *18*(1), 357-370. https://doi.org/10.5194/acp-18-357-2018

Rindelaub, J. D., Craig, R. L., Nandy, L., Bondy, A. L., Dutcher, C. S., Shepson, P. B., & Ault, A. P. (2016). Direct Measurement of pH in Individual Particles via Raman Microspectroscopy and Variation in Acidity with Relative Humidity. *J. Phys. Chem. A*, *120*(6), 911-917. https://doi.org/10.1021/acs.jpca.5b12699

Seinfeld, J. H., & Pandis, S. N. (2016). *Atmospheric chemistry and physics: from air pollution to climate change* (3 ed.). John Wiley & Sons.

Tao, Y. (2020). *Identification of Major Factors Influencing Aerosol pH and the Quantitative Relationship between pH and Ammonia Gas/Particle Partitioning* University of Toronto]. University of Toronto TSpace. https://hdl.handle.net/1807/103788

Tao, Y., & Murphy, J. G. (2019). The sensitivity of PM2.5 acidity to meteorological parameters and chemical composition changes: 10-year records from six Canadian monitoring sites. *Atmos. Chem. Phys.*, *19*(14), 9309-9320. https://doi.org/10.5194/acp-19-9309-2019

Valerino, M. J., Johnson, J. J., Izumi, J., Orozco, D., Hoff, R. M., Delgado, R., & Hennigan, C. J. (2017). Sources and composition of PM2.5 in the Colorado Front Range during the DISCOVER-AQ study. *Journal of Geophysical Research-Atmospheres*, *122*(1), 566-582. https://doi.org/10.1002/2016jd025830

Vasilakos, P., Russell, A., Weber, R., & Nenes, A. (2018). Understanding nitrate formation in a world with less sulfate. *Atmos. Chem. Phys.*, *18*(17), 12765-12775. https://doi.org/10.5194/acp-18-12765-2018

Weber, R. J., Guo, H., Russell, A. G., & Nenes, A. (2016). High aerosol acidity despite declining atmospheric sulfate concentrations over the past 15 years [Letter]. *Nature Geoscience*, *9*(4), 282-285. https://doi.org/10.1038/ngeo2665

Zheng, G., Su, H., Wang, S., Andreae, M. O., Pöschl, U., & Cheng, Y. (2020). Multiphase buffer theory explains contrasts in atmospheric aerosol acidity. *Science*, *369*(6509), 1374. https://doi.org/10.1126/science.aba3719