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High aerosol acidity despite declining atmospheric sulfate concentrations over the past 15 years

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Particle acidity affects aerosol concentrations, chemical composition and toxicity. Sulfate is often the main acid component of aerosols, and largely determines the acidity of fine particles under 2.5 µm in diameter, $PM_{2.5}$. Over the past 15 years, atmospheric sulfate concentrations in the southeastern United States have decreased by 70%, whereas ammonia concentrations have been steady. Similar trends are occurring in many regions globally. Aerosol ammonium nitrate concentrations were assumed to increase to compensate for decreasing sulfate, which would result from increasing neutrality. Here we use observed gas and aerosol composition, humidity, and temperature data collected at a rural southeastern US site in June and July 2013 (ref. 1), and a thermodynamic model that predicts pH and the gas–particle equilibrium concentrations of inorganic species from the observations to show that $PM_{2.5}$ at the site is acidic. pH buffering by partitioning of ammonia between the gas and particle phases produced a relatively constant particle pH of 0–2 throughout the 15 years of decreasing atmospheric sulfate concentrations, and little change in particle ammonium nitrate concentrations. We conclude that the reductions in aerosol acidity widely anticipated from sulfur reductions, and expected acidity-related health and climate benefits, are unlikely to occur until atmospheric sulfate concentrations reach near pre-anthropogenic levels.

Trends of decreasing sulfur dioxide (SO_2) and sulfate aerosol have been observed throughout the United States (ref. 2) and are largely attributable to emission reductions from coal-fired electrical generating units through scrubbing and fuel switching. These trends are expected to endure as additional controls on SO_2 are put in place to continue the decline of $PM_{2.5}$ mass. In contrast, the source of the main fine-particle acid-neutralizing agent, gas-phase ammonia (NH_3), is largely linked to agricultural activities, which have been relatively steady and are expected to remain so. These trends have led to a long-standing and continuing belief that the aerosol will become increasingly neutral, shifting inorganic aerosol composition from ammonium sulfate to ammonium nitrate and minimizing the effectiveness of SO_2 reductions on $PM_{2.5}$ mass control[3–8]. This has wide-ranging ramifications, from changing the emphases on what emission sources to control (for example, agricultural) to protect human health[9] to effects on aerosol radiative forcing[10]. Other environmental impacts linked to particle pH are also expected to change. For example, lower pH more effectively converts ubiquitous isoprene emissions by forested regions to $PM_{2.5}$ through heterogeneous acid-catalysed reactions[11]. Low pH increases solubility of metals associated with mineral dust and anthropogenic sources, which can be either ecosystem nutrients[12], or have detrimental health impacts through *in vivo* generation of reactive oxygen species[13]. Particle strong acidity has also been directly linked to adverse respiratory effects[14,15].

Despite large investments in sulfur emission reductions, we show that the acid/base gas–particle system in the southeastern United States is buffered by the partitioning of semivolatile NH_3, making it insensitive to changing SO_2 levels. Counter to expectations, acidic pH effects on air quality will therefore remain largely unchanged. Although our analysis focuses on the southeastern United States, it serves as a model, demonstrating the need for detailed thermodynamic analyses at locations globally to accurately evaluate the effects of sulfate reductions on particle acidity and aerosol composition.

To assess if decreasing sulfate leads to substantial changes in aerosol pH, we investigate the sensitivity of pH in the southeastern United States to changes in sulfate (SO_4^{2-}) and gas-phase ammonia (NH_3) levels, focusing on summertime data from a rural southeastern background site, Centreville (CTR). The historical breadth of data collected at CTR, and the detailed observations of key aerosol and gas phase species measured during a recent intensive study at the site (SOAS), make it ideal for thermodynamic analyses to predict and evaluate pH at high temporal resolution and for comparisons to historical trends.

A detailed pH calculation that involves both gas and aerosol composition data was performed using average conditions from a subset of the CTR SOAS experiment (11 June to 23 June 2013). This time period was selected because it excludes periodic precipitation and dust events, providing representative conditions consistent with the mean summertime aerosol state in the region. ISORROPIA-II-predicted NH_3 agreed with independently measured concentrations (Fig. 1), demonstrating that the thermodynamic analysis accurately represents the aerosol state, as deviations in predicted pH would lead to large biases in predicted NH_3.

Measurements at various SEARCH air-quality monitoring network sites throughout the southeast show that annual mean SO_4^{2-} concentrations have dropped substantially from 1999 to 2014 , with concentrations going from roughly 6 to 2 $\mu g\, m^{-3}$ (ref. 16). Historical NH_3 concentrations are not as well known; however, data from SEARCH sites[8] and the Ammonia Monitoring Network (AMoN) (http://nadp.sws.uiuc.edu/amon) show steady overall concentrations going back to 2004. Between 2008 and 2014, CTR mean summer concentration was 0.23 $\mu g\, m^{-3}$, similar to measurements at CTR during SOAS (mean: 0.36 $\mu g\, m^{-3}$; ref. 17). Ammonia at other

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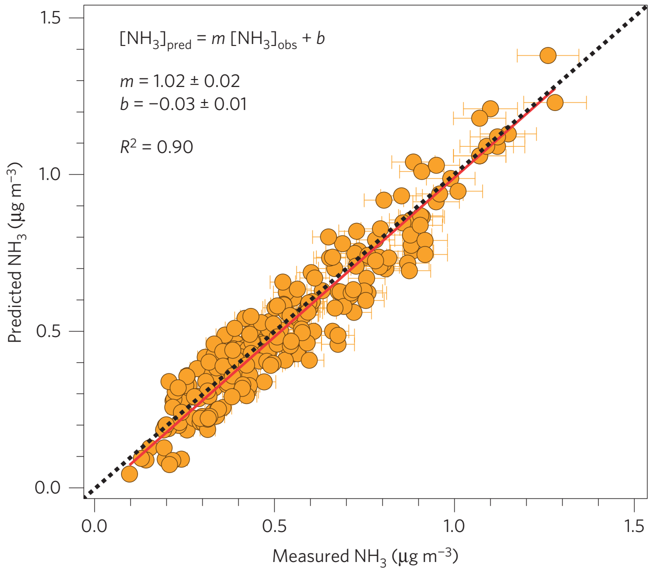

Figure 1 | Evaluation of the thermodynamic model. Comparison of measured NH_3 to ISORROPIA-II-predicted concentrations. Data are from SOAS (that is, SEARCH CTR site) for measurements between 11 June and 23 June 2013. NH_3 was measured via a chemical ionization mass spectrometer (CIMS; ref. 17). Orthogonal regression and the uncertainty in the measured NH_3 1 h-avg data (10%) are shown. Fit parameter uncertainties are for 95% confidence intervals. The good agreement validates the model predictions of pH.

sites in the southeast generally ranged between 0.1 and 2 µg m^{-3}, with highest levels observed at sites more influenced by agricultural activities (for example, at Yorkville, a rural SEARCH site, mean NH_3 is 1.74 µg m^{-3}). A mass balance analysis indicates that NH_3 concentrations are directly driven by NH_3 emission rates (see Methods). Given this, and that emissions are relatively steady[18], NH_3 concentrations have probably been at similar levels even further into the past.

Conceptual model

To test if these trends imply that the aerosol is becoming less acidic we first consider a simplified scenario of an isolated ammonium sulfate aqueous particle. At the average SOAS conditions, for this particle the equilibrium NH_3 vapour concentration is approximately 160 µg m^{-3} (220 ppbv) and pH is near 3 (see Methods for description of calculations). However, for ammonium bisulfate the equilibrium NH_3 concentration drops sharply to approximately 0.06 µg m^{-3} (0.08 ppbv), and pH is near 0. Because typical observed NH_3 concentrations range between 0.1 and 2 µg m^{-3}, ambient NH_3 concentrations will rarely ever reach the 160 µg m^{-3} needed for equilibrium with pure ammonium sulfate, meaning that it will almost never exist. However, NH_3 will always be present in the gas phase, even at very low pH. Furthermore, the sharp drop in equilibrium NH_3 when going from $(NH_4)_2SO_4$ to $(NH_4)HSO_4$ (160 to 0.06 µg m^{-3}) with a pH change of only 3 to 0, independent of sulfate concentrations, also demonstrates the low sensitivity of pH to NH_3 concentrations.

Now consider an ammonium sulfate solution that is aerosolized into pure air. The aerosol would reach equilibrium by some of the ammonia volatilizing, leaving an aerosol of mixed $(NH_4)_2SO_4$–NH_4HSO_4 with a pH between 0 and 3, and some ammonia in the gas phase. If the volume of air were very large compared to the amount of ammonium sulfate originally present, the resulting aerosol would be predominantly ammonium bisulfate. (Ammonium sulfate molar ratios observed in the southeastern United States are in the range of 1.5 to 1.8, which is discussed further below.) Although conceptually insightful, the full thermodynamic model must be run because pure aerosol species in isolation do not exist and a quantified pH is needed to assess the impacts of acidity.

Sensitivity analyses with a full thermodynamic model

We expand on the historical ranges of both NH_3 and SO_4^{2-} for more comprehensive sensitivity analyses. Sulfate and total ammonia (gas + particle) were independently varied over two orders of magnitude and used as input to ISORROPIA-II. The resulting predicted equilibrium pH is shown in Fig. 2. As seen above, these results indicate a very weak sensitivity of pH to a wide range of SO_4^{2-} and NH_3, suggesting that the observed decrease in SO_4^{2-} should have little influence on pH. Our predictions are consistent with the historical summertime observations at CTR. Trends in fine-particle SO_4^{2-} and NH_4^+ and gas-phase NH_3 are shown in Fig. 3, and are similar to the general trends of the southeast[8,16], and probably much of the eastern United States (ref. 2). pH estimated from the CTR historical aerosol ionic composition data set also demonstrates that summertime pH has remained remarkably constant and low (between 0 and 1) throughout the past 15 years, similar to the range of roughly 0 and 2 predicted in the sensitivity analyses.

A further assessment of the thermodynamics can be gained from ammonium-to-sulfate molar ratios, R_{SO_4} (see Methods). Hidy[16]

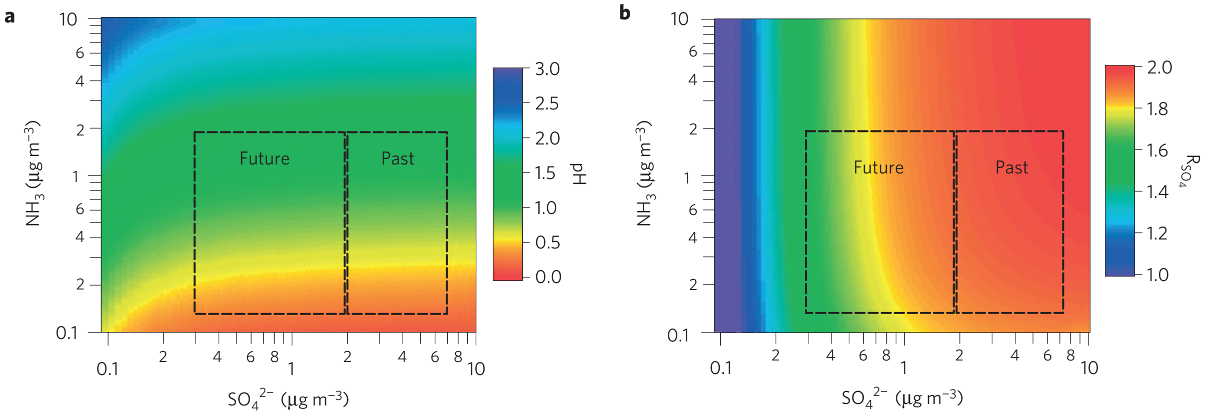

Figure 2 | Sensitivity of $PM_{2.5}$ pH and R_{SO_4} to gas-phase ammonia (NH_3) and $PM_{2.5}$ sulfate (SO_4^{2-}) concentrations. The results are predictions from a thermodynamic analysis assuming equilibrium between the gas and particle phases for typical summer conditions in the southeastern United States. Boxes define estimated concentration ranges over the previous 15 years and ranges expected in the future. R_{SO_4} is $[(NH_4^+ - NO_3^-)/SO_4^{2-}]$.

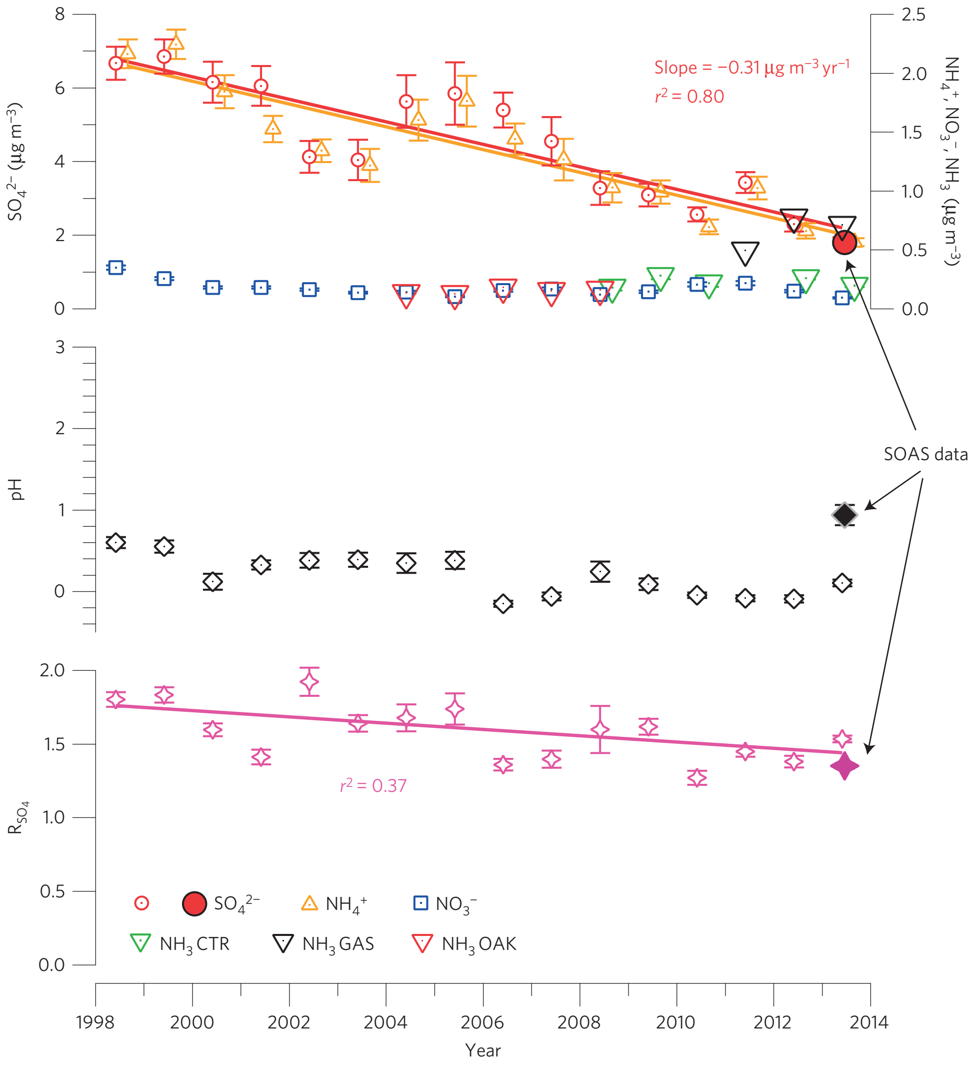

Figure 3 | Mean summer (June–August) trends in $PM_{2.5}$ composition, NH_3, R_{SO_4} and predicted $PM_{2.5}$ pH at the SEARCH-CTR site. NH_3 data are from the SEARCH rural sites Centreville (CTR, Alabama) and Oak Grove (OAK, Mississippi), and AMON Georgia Station (GAS, Georgia) site. SOAS mean data (1 June to 15 July 2013) are also plotted. Error bars represent data ranges (standard errors). pH was estimated with ISORROPIA-II run in the forward mode without gas-phase species input, resulting in pH systematically low by approximately one unit[1]. Uncertainties: ions ± 15%, molar ratios ± 26%, NH_3 ±15 to 40%.

reports R_{SO_4} has ranged roughly between 1.5 and 1.8 at sites in the southeast, corresponding to a mixture of ammonium sulfate and ammonium bisulfate as the dominant salts. Surprisingly, R_{SO_4} decreased by 0.01 to 0.03 units per year over the past 15 years. This is counterintuitive, as it shows that, as sulfate is reduced and the NH_3 to neutralize it remains constant, the aerosol is increasingly enriched in acidic ammonium bisulfate, whereas the expectation is that the aerosol should become more neutral over time (that is, R_{SO_4} increasing and approaching 2). CTR R_{SO_4} follows a similar decreasing trend (Fig. 3) and the thermodynamic sensitivity analysis (Fig. 2b) is consistent with these observations.

All these results can be explained by the non-volatility of sulfate and semivolatility of ammonia, meaning that only NH_3 moves to establish equilibrium between the condensed aqueous and gas phase. For example, decreasing R_{SO_4} occurs because particle-phase ammonium roughly tracks SO_4^{2-} (Fig. 3), so at lower SO_4^{2-} there is less ammonium available when establishing equilibrium with gas-phase NH_3. During equilibration, ammonium (NH_4^+) is lost to the gas-phase (NH_3), releasing H^+ in the aerosol and decreasing R_{SO_4}. Because a larger relative loss in ammonium occurs at lower SO_4^{2-}, R_{SO_4} is lower. The semivolatility of ammonium is also responsible for the remarkably weak sensitivity of pH to SO_4^{2-}. Further evidence is that pH begins to rise in the sensitivity analyses (Fig. 2a) for SO_4^{2-} below roughly 0.3 μg m^{-3}; the thermodynamic analysis suggests this is due to association of SO_4^{2-} with other non-volatile cations that starts to mitigate the buffering effect of NH_3 partitioning, significantly increasing pH (see Supplementary Extended Data Fig. 1).

The sensitivity analysis (Fig. 2a) does show a pH increase with increasing NH_3, but it is relatively weak, a consequence of the buffering effect of semivolatile NH_3 partitioning. For SO_4^{2-} between 0.1 and 10 μg m^{-3}, it is not until NH_3 is over 10 μg m^{-3} (14 ppbv) before pH approaches 2.5; the approximate minimum pH at which ammonium nitrate begins to form for conditions of this study (see Supplementary Extended Data Fig. 2). In summary, for typical summer conditions the observed trends in pH and R_{SO_4} are expected and due to gas–particle thermodynamic equilibrium, along with relatively constant NH_3 levels that have been below a few μg m^{-3} over the past 15 years.

Future pH

The thermodynamic sensitivity analyses were continued for SO_4^{2-} down to 0.1 μg m^{-3}, levels characteristic of remote regions[19]. As emissions of NH_3 are decoupled from SO_4^{2-}, linked mainly to agricultural and biogenic activities, in the foreseeable future one may expect this source to remain largely flat, or modestly increase as agricultural production follows population increases. This indicates that future gas-phase NH_3 concentrations will not deviate considerably from current levels[8]. The area of expected future conditions in Fig. 2 shows that summertime pH will remain in the 0 to 2 range, similar to current levels and those of the past 15 years. The system insensitivity to NH_3 implies that it is a poor indicator of fine aerosol pH. Furthermore, if the aerosol is in an aqueous phase the presence of NH_3 does not necessarily imply a neutral aerosol, as often assumed[20], as some NH_4^+ always needs to volatilize to achieve equilibrium.

The sensitivity analysis also predicts changes in gas/particle portioning ratios with changing SO_4^{2-} and NH_3. Over the broad SO_4^{2-} range of 0.1 to $10\,\mu g\,m^{-3}$, the fraction of NH_3 in the gas phase relative to total (gas + particle) varies from about 90 to 10%, indicting coupling of gas–particle ammonia concentrations across this SO_4^{2-} range. In contrast, nitric acid is predicted to remain largely in the gas phase, unaffected by SO_2 controls owing to the predicted low pH. Nitrate aerosol is expected only once pH is over ~2 to 3, and so minimal particle-phase inorganic nitrate is expected for typical summer conditions; neither in the past as SO_4^{2-} has decreased, and verified by the historical data (Fig. 3), nor for some time into the future, given expected pH ranges (Fig. 2). If there are no significant changes in future non-volatile cation levels in the fine aerosol mode (for example, increases in mineral dust due to land use changes or desertification, discussed in Supplementary Information), summertime $PM_{2.5}$ in the southeastern United States will remain highly acidic until average sulfate levels approach those of very clean remote continental sites (~$0.3\,\mu g\,m^{-3}$; refs 19,21) and particulate nitrate will not become an increasing air-quality issue for a long time into the future—counter to expectations.

Although our analysis focuses on the southeastern United States, it applies to all locations that are impacted by SO_2 emissions and which lack major sources of non-volatile cations (for example, sea-salt or mineral dust); conditions commonly found in many regions globally. Although reductions in sulfur dioxide (SO_2) and oxides of nitrogen (NO_x) will reduce sulfate, nitrate and ammonium aerosol concentrations, leading to improved air quality, we show that fine particles are highly acidic and are likely to remain so despite substantial sulfate reductions. Furthermore, particle pH must be explicitly considered to accurately gauge its impacts on heterogeneous chemical processes, particle composition, mass concentrations and toxicity.

Methods

Methods and any associated references are available in the online version of the paper.

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Author contributions

R.J.W. initiated the investigation. H.G. and A.N. performed the thermodynamic modelling analyses. A.G.R. provided the mass balance analysis. All authors extensively discussed the concepts, commented on the manuscript and contributed to writing the manuscript.

Additional information

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to R.J.W.

Competing financial interests

The authors declare no competing financial interests.

Methods

The site. Centreville is part of the SEARCH (Southeastern Aerosol Research and Characterization) air-quality monitoring network[8] and is located in rural Alabama (CTR; 32.90289° N, 87.24968° W; altitude: 126 m, Brent, Alabama). It was also the location of the intensive multi-investigator Southern Oxidant Aerosol Study (SOAS, June 1 to July 15, 2013). We have reported on a detailed analysis of pH as part of SOAS and have shown that pH throughout the southeast is fairly uniform[1], similar to levels at CTR. More information on the site, instrumentation, and thermodynamic calculations, including an uncertainty analysis, can be found in Guo and colleagues[1].

Thermodynamic model. Direct and accurate measurement of particle pH of the atmospheric aerosol is not possible at present. Measurements of semivolatile partitioning of key inorganic species (such as ammonia/ammonium, nitric acid/nitrate) coupled with thermodynamic models are the best approaches for predicting particle pH with a high degree of accuracy[22]. For this study we use ISORROPIA-II (refs 23,24), which computes the equilibrium composition of an NH_4^+–SO_4^{2-}–NO_3^-–Cl^-–Na^+–Ca^{2+}–K^+–Mg^{2+}–water inorganic aerosol. Proxies for pH, such as ammonium-to-sulfate molar ratios, NH_4^+/SO_4^{2-}, have been used in the past. Although the molar ratio is commonly used as a measure of aerosol acidity, it is not uniquely related to pH, which is the parameter that truly describes acidity and its impacts[22]. Here we more narrowly define the ammonium-to-sulfate molar ratios as ammonium minus nitrate to sulfate molar ratio; $(NH_4^+-NO_3^-)/SO_4^{2-}$ and refer to this ratio as R_{SO_4}. This is preferred to the simpler ammonium-to-sulfate molar ratio (NH_4^+/SO_4^{2-}) as it excludes NH_4^+ associated with NO_3^- when calculating ratios based on bulk composition data (for example, $PM_{2.5}$), because ammonium sulfate and ammonium nitrate are typically associated with different-sized particles.

pH is defined as the hydrogen ion activity in an aqueous solution[25] as $pH = -\log(\gamma x_{H^+})$, where γ is the hydrogen ion activity coefficient and x_{H^+} is the aqueous solution mole fraction of dissociated H^+. ISORROPIA-II computes the particle liquid water content due to water uptake by inorganic species, phase partitioning and chemical speciation, and makes the simplifying assumption that the hydrogen ion activity is unity ($\gamma = 1$). Details on how the model was run, an extensive uncertainty analyses, and predictions of pH at various sites in the southeast, are discussed in Guo and colleagues[1]. In applying ISORROPIA-II, we assumed no compositional dependence on particle size, treating the measured chemical constituents as bulk $PM_{2.5}$ properties, and that the aerosol was internally mixed and always a single aqueous phase that contained the inorganic species, without phase separations that could affect pH (along with partitioning of semivolatile inorganic species). The validity of these assumptions has been evaluated. We have shown that the fine particles contain significant levels of liquid water (water mass typically ranged from 1 to 5 $\mu g\,m^{-3}$; ref. 1). Existence of one organic–inorganic phase is reasonable given that the measured organic aerosol oxidation state (average O/C ratio of ~0.7; ref. 26) and RH (mean ± s.d. of 74 ± 16%; ref. 1) for this study are typically at levels for which separate phases are not observed[27]. pH calculated under these assumptions (bulk properties, no phase separations, dissolved components in equilibrium with the gas phase) is supported by the ability of ISORROPIA-II to reproduce independently measured gas-phase NH_3 concentrations (Fig. 1). Furthermore, multiple studies in the past have shown the ability of ISORROPIA-II (under similar assumptions to what are used here) to reproduce the observed behaviour of semivolatile inorganic aerosol in the southeast[28] and at other locations[29].

For the conceptual analysis into a lack of sensitivity of aerosol pH to gas-phase ammonia (NH_3), we ran ISORROPIA in reverse (open) mode to predict equilibrium concentrations of NH_3 above a pure aqueous ammonium sulfate ($(NH_4)_2SO_4$) particle and pure aqueous ammonium bisulfate ($(NH_4)HSO_4$) particle. In reverse mode, only particle-phase data is input to ISORROPIA, along with temperature and RH. Essentially constant NH_3 and particle pH values (see main text) are obtained for a wide range of input sulfate concentrations (for example, 0.1 to 10 $\mu g\,m^{-3}$). (Note, once sulfate is specified, the corresponding NH_4^+ concentrations to achieve a molar ratio of 1 or 2 are determined.) Average SOAS ambient conditions ($T = 298$ K, RH = 74%) were used in this analysis.

The approach for generating the contour plots of Fig. 2 is as follows. Average SOAS data collected between 11 June and 23 June 2013 ($T = 297.9$ K, RH = 73.8%, $Na^+ = 0.03\ \mu g\,m^{-3}$, $NO_3^- = 0.08\ \mu g\,m^{-3}$, $Cl^- = 0.02\ \mu g\,m^{-3}$), along with a selected sulfate concentration, are input to ISORROPIA-II run in forward mode. Total ammonia (gas + particle) is left as the free variable. The equilibrium concentrations of various components (for example, gas-phase NH_3, and particle-phase NH_4^+, SO_4^{2-}, and NO_3^-) and particle pH (along with other variables) are predicted by ISORROPIA-II. Data for the contour plots are generated by varying sulfate from 0.1 to 10 $\mu g\,m^{-3}$.

Ammonia mass balance. Ammonia emissions can be linked to ambient concentrations through mass balance analysis. Boundary layer ammonia levels can be estimated from emissions and losses by:

$$\frac{d[NH_3]}{dt} = E_{NH_3} - \frac{v_d^{NH_3}}{h}[NH_3] - \frac{v_d^{NH_4^+}}{h}[NH_4^+] \qquad (1)$$

where $[NH_3]$ and $[NH_4^+]$ are the concentrations of gas ammonia and fine-particle ammonium, E_{NH_3} the gas-phase NH_3 emission rate, $v_d^{NH_3}$ the gas-phase deposition velocity, $v_d^{NH_4^+}$ the particle-phase deposition velocity, and h the boundary layer mixed depth. Because average values are being considered here, we assume steady state, in which case emissions are balanced by deposition losses. It follows then that for sulfate concentrations dropping below current levels (~7 $\mu g\,m^{-3}$), loss of ammonia by deposition is largely controlled by gas-phase losses, because $v_d^{NH_3}$ is roughly an order of magnitude larger then $v_d^{NH_4^+}$, and ambient concentrations of NH_4^+ and NH_3 are comparable[1]. For example, the dry deposition velocity of NH_3 is about 1–2 $cm\,s^{-1}$ over forests, agricultural, or mixed-use land, and 10 times that of ammonium[30,31]. For sulfate levels below ~2 $\mu g\,m^{-3}$ (NH_4^+ ~0.5 $\mu g\,m^{-3}$, that is, current levels, Fig. 3) and NH_3 concentration of 0.1 to 1, the last term is relatively small and so ambient levels of NH_3 are largely controlled by emissions, such that $[NH_3] \cong (hE_{NH_3}/v_d^{NH_3})$. This shows that for the recent past, and into the future, gas-phase NH_3 concentrations are directly related to gas-phase NH_3 emissions rates.

Data availability. pH and R_{SO_4} data are available at http://www.aerosols.eas.gatech.edu/Weber_Nature_Figure_data.xlsx.

Code availability. ISORROPIA-II is available at: http://isorropia.eas.gatech.edu.

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