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Historical Changes in Seasonal Aerosol Acidity in the Po Valley (Italy) as Inferred from Fog Water and Aerosol Measurements

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ABSTRACT: Acidity profoundly affects almost every aspect that shapes the composition of ambient particles and their environmental impact. Thermodynamic analysis of gas-particle composition datasets offers robust estimates of acidity, but they are not available for long periods of time. Fog composition datasets, however, are available for many decades; we develop a thermodynamic analysis to estimate the ammonia in equilibrium with fog water and to infer the pre-fog aerosol pH starting from fog chemical composition and pH. The acidity values from the new method agree with the results of thermodynamic analysis of the available gas-particle composition data. Applying the new method to historical (25 years) fog water composition at the rural station of San Pietro Capofiume (SPC) in the Po Valley (Italy) suggests that the aerosol has been mildly acidic, with its pH decreasing by 0.5−1.5 pH units over the last decades. The observed pH of the fog water also increased 1 unit over the same period. Analysis of the simulated aerosol pH reveals that the aerosol acidity trend is driven by a decrease in aerosol precursor concentrations, and changes in temperature and relative humidity. Currently, NO_x controls would be most effective for $PM_{2.5}$ reduction in the Po valley both during summer and winter. In the future, however, seasonal transitions to the NH_3-sensitive region may occur, meaning that the NH_3 reduction policy may become increasingly necessary.

KEYWORDS: *aerosol pH, fog water chemical composition, gas-particle partitioning, thermodynamics*
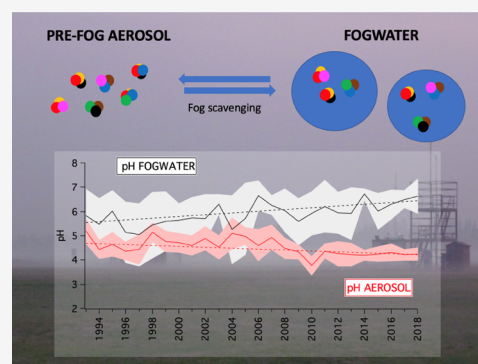
1. INTRODUCTION

Aerosol acidity is a key driver of many important atmospheric processes,[1,2] affecting partitioning of semivolatile species, SOA formation, and solubilization of trace metals, with important implications for air quality, the health of human and ecosystems, and climate. Despite its importance, the direct measurement of the pH of atmospheric aerosol is highly challenging, with only a few techniques available for its determination.[3−5] Indirect proxies (e.g., aerosol ionic molar ratios) have been used extensively in the past to represent particle acidity, although their link with pH is largely qualitative.[2,6,7] The most reliable estimates of aerosol acidity to date are obtained by thermodynamic analysis of ambient observations.[6−8] In this approach, aerosol thermodynamic models (such as ISORROPIA-II[9]) are applied to determine the concentrations of species in the gas and aerosol phases that control the water uptake of the aerosol. If the observed gas-particle partitioning of species sensitive to aerosol pH (e.g., $NH_3(g)/NH_4^+$, $HNO_3(g)/NO_3^-$) and liquid water content (W) are sufficiently captured by the thermodynamic model, the pH calculated from the thermodynamic model would be a good estimate of the true value.[5]

Using thermodynamic analysis, datasets of aerosol acidity are appearing with increasing frequency (see the review by Pye et al.[2]); however, their number and temporal span are limited compared to a large number of PM composition datasets available because the required concurrent measurements of the gas-phase concentrations of NH_3 and/or HNO_3 are often unavailable. In most cases, even if it may not be the case for dust or sea salt particles, NH_3 concentration is enough to derive aerosol acidity, as it acts as a buffer that controls aerosol pH.[1,10] In the absence of NH_3 data, one can still obtain robust pH estimates if NO_3^-/HNO_3 observations are available.[11] If neither HNO_3 nor NH_3 observations are available, the pH estimates can still be obtained, albeit with a constrained (but non-negligible) bias.[8,12]

To date, thermodynamic analysis has been applied exclusively to aerosol−gas-phase composition data. This approach is the most straightforward, as the observations provide the direct input required by the thermodynamic models to calculate semivolatile partitioning and the aerosol pH. Other nonconventional datasets, however, may provide aerosol pH with an appropriately formulated thermodynamic analysis. Fog water data offer such potential, as fogs—which act like natural "mist chamber" samplers—tend to scavenge significant fractions of aerosol mass and soluble vapors such as NH_3, HNO_3, and HCl. Gilardoni et al.[13] showed that aerosol down to about 100 nm was scavenged by fog droplets in the Po Valley—so most of the mass that controls aerosol pH was contained in the fog water. The fog water pH and liquid water content can also be directly measured, allowing for estimations of gas-phase aerosol precursors (the main ones being NH_3, HNO_3, and HCl[14]). Combining this fog water and gas-phase information allows for a thermodynamic analysis that can be used to constrain the pre-fog aerosol acidity. A combined aerosol−fog water thermodynamic analysis is also important to understand the role of aerosols in fogs as media for the production of secondary organic aerosol, especially during intense haze events.[15]

In this study, we evaluate the potential of using the fog water ionic composition data to estimate the pH of the preexisting aerosol. The method is evaluated using the data collected in the Po Valley of Italy. Concurrent measurements of aerosol and gas-phase composition before fog events are also used to estimate the aerosol pH and are compared against the fog-water-derived values. The fog-water-based method is then applied to the full dataset, which covers a period of over 25 years.[12] The resulting aerosol pH trend is then compared against the fog water pH trend, and its links to the emissions of aerosol precursors (i.e., SO_2, NO_x, and NH_3) and meteorological parameters (T and RH) are explored.

2. EXPERIMENTAL METHODS

2.1. Fog Water Collection and Analysis. Fog water is collected systematically at the field station of San Pietro Capofiume (SPC) since 1989 (from November to March). A series of intensive fog campaigns also took place in SPC during the 1980s.[17−20] Fog water is sampled using an automated active string collector, extensively described by Fuzzi et al.[21] The collector consists of a system in which fog droplets, carried by the air stream created by a fan located at the rear part of a short wind tunnel, are forced to impact on a series of strings. The impacted droplets then coalesce with each other and drain off the stainless-steel strings into a funnel to eventually be collected in a sampling bottle. The airflow through the tunnel is approximately 17 m^3 min^{-1} with a 50% collection efficiency of individual string at approximately 3 mm droplet radius.

A Particulate Volume Monitor PVM-100 is used to measure the liquid water content of the fog (LWC_f) with a time resolution of 1 min. This monitor is used to activate the string collector when LWC_f exceeds 0.08 g m^{-3}. This threshold corresponds to visibility of approximately 200 m^{22} and the fog is considered dense (the meteorological definition of fog is visibility less than 1 km).

Direct pH measurements of the liquid fog samples are carried out using a Crison micropH 2002 pH meter: this measurement is done in the laboratory of ISAC-CNR (at Bologna, about 40 km from SPC) as soon as the sample arrives

from the field; usually, a short trip by car (30−40 min of transport). If for any reason the time is longer, the fog sample is refrigerated in the fridge or directly outside (stored in a corked sampling bottle, on the terrace of the laboratory) for at least 60 min to rebalance the temperature as much as possible with that of the ambient air. Fog water samples are filtered (47 mm quartz-fiber filters) within a few hours after collection to remove any suspended particles. The samples are then stored frozen until the chemical analysis. Liquid samples are analyzed for inorganic ions (NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, SO_4^{2-}) and low molecular weight organic acids (acetate, formate, methanesulfonate, and oxalate) by ion chromatography.[23] The results of this chemical characterization and the temporal trends in the observed chemical and physical parameters were presented by Giulianelli et al.[16] As reported in Giulianelli et al.,[16] analytical problems affected the chromatographic data from 1989/1990 to 1992/1993 and these samples were excluded from our analysis. A total of 577 fog water samples were analyzed from November 1993 to December 2018, with an annual median number of samples of 23 (4−37). The smallest number of samples corresponds to the central years of the time series (2004−2006), for which the statistics should be considered less robust.

2.2. PM$_{2.5}$ and Ammonia Measurements. Daily $PM_{2.5}$ and gaseous ammonia (NH_3) measurements are carried out by the Regional Agency for Prevention, Environment, and Energy (ARPAE) of Emilia-Romagna, Italy. The $PM_{2.5}$ filter sampling started in the framework of the Supersito project (www.arpae.it/supersito) from November 2011 and continues to date following the protocol described by Ricciardelli et al.[24] $PM_{2.5}$ daily samples are collected at SPC on quartz fiber filters (PALL Tissu Quartz 2500 QAO-UP 2500 47 mm filters) for the analysis of the major inorganic ions (NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, SO_4^{2-}). After the collection with a Single Channel Monitor (SWAM FAI Rome, Italy) operating at the standard flow rate of 38.3 L min^{-1} (EN12341), the samples are extracted in 10 mL of MilliQ water, sonicated for 15 min, filtered through 0.45 mm cellulose acetate filters, and then injected into an Ion Chromatography system (DIONEX, California). Gaseous ammonia (NH_3) hourly measurements are available at SPC starting from August 2017, thanks to a chemiluminescence ammonia analyzer (model 201E, Teledyne-API, San Diego, CA) of the air quality network of ARPAE Emilia-Romagna (following a standard certified QA/QC procedure ISO9001:2015, www.arpae.it, Section S1).

2.3. Meteorological Data. Daily maximum, minimum, and mean values for T and RH are available at SPC since 1993. Since 2007, hourly data are available by the Hydro-Meteo-Climate Service of ARPAE-ER (simc.arpae.it/dext3r/). T and RH measurements are validated against the data measured at SPC continuously by a VAISALA meteorological station.

3. MODELING METHODS

3.1. Thermodynamic Analysis of Fog Water Composition to Obtain Pre-Fog Aerosol pH. The ISORROPIA-II (version 2.3) aerosol thermodynamic model[6] (http://isorropia.epfl.ch) is used to calculate the composition and phase state of a K^+−Ca^{2+}−Mg^{2+}−NH_4^+−Na^+−SO_4^{2-}−NO_3^-−Cl^-−water inorganic aerosol in thermodynamic equilibrium with gas-phase precursors. ISORROPIA-II has been extensively used to predict the liquid water content and pH for inorganic aerosol.[1,8,12,25−27] Similar to previous studies, the definition of pH used here is

$$\text{pH} = -\log_{10} \gamma_{H^+} H_{aq}^+ = -\log_{10} \frac{1000 \gamma_{H^+} H_{air}^+}{W_i + W_o}$$

$$\cong -\log_{10} \frac{1000 \gamma_{H^+} H_{air}^+}{W_i} \tag{1}$$

where γ_{H^+} is the hydronium ion activity coefficient (here, assumed unity), H_{aq}^+ (mol L^{-1}) is the hydronium ion concentration in the aqueous phase of the aerosol, H_{air}^+ (μg m^{-3}) is the hydronium ion concentration per volume of air, and W_i and W_o (μg m^{-3}) are particle water concentrations associated with the aerosol-inorganic and -organic species, respectively. The pH used here is consistent with the pH$_F$ definition of Pye et al.[2] In this work, we neglect the contribution of water from the organic species and their overall effect on the water activity and pH. Guo et al.,[8] Song et al.,[7] Vasilakos et al.,[28] and Battaglia et al.[29] evaluated this assumption and found the organic species to have a secondary effect on the aerosol pH, being somewhere between 0.15 and 0.3 pH units. So, since the organic aerosol hygroscopicity is not measured in our study and given that neglecting W_o appears to have only a minor impact on the pH characterization, we determine pH only considering W_i.

We used ISORROPIA-II in the partitioning ("forward") mode for metastable aerosol. In this configuration, the model is used to calculate the equilibrium partitioning given the total concentration (gas plus particles) of various species together with RH and T as input. Considering that the fog scavenging efficiency of inorganic species is generally higher than 70% and shows little variability,[13,30] here we apply the partitioning mode using the ionic composition of fog water (as a proxy of the particle composition and amount) and the corresponding gaseous ammonia concentrations, as estimated in Section 3.2.

The total (gas and aerosol) concentration of species i in the pre-fog atmosphere ($C_{i,air}$, μg m^{-3}) is obtained by multiplying their concentration in fog water ($C_{i,fog}$, μg mL^{-1}) with the liquid water content of the fog (LWC$_{air}$, mL m^{-3})

$$C_{i,air} = C_{i,fog} \text{LWC}_f \tag{2}$$

Given the relatively high pH of the fog water, some ammonia is present in the gas phase; its concentration is estimated based on its measured fog water concentration and pH (Section 3.2). This is added to the concentration calculated using eq 2. A similar inference of gas-phase HNO$_3$ and HCl is deemed unnecessary in this case, given the high value of pH and LWC$_f$ of fogs in SPC.[26]

We test in Section 4.1 the reliability of our approach on a limited subset of data for which parallel measurements of PM$_{2.5}$ and NH$_3$(g) are available, comparing NH$_3$(g)/NH$_4^+$(p) predictions with the measured ammonia gas-particle partitioning. We also evaluate the impact of neglecting gaseous ammonia from the calculation, applying the model even with just aerosol-phase data as already done in previous studies.[6]

3.2. Estimating Gaseous Ammonia in Fogs. Although fogs scavenge most of the aerosol and a large fraction of the water-soluble gases of interest for pH determination (namely, NH$_3$ and HNO$_3$), a portion remains in the gas phase in quasiequilibrium with the fog water. If the atmospheric concentration of gaseous ammonia in fog (NH$_{3(fog)}$) is known, it can be included in the thermodynamic analysis. To determine NH$_{3(fog)}$, we first assume that NH$_3$ is in equilibrium with the fog water NH$_4^+$, and then correct to account for any apparent departure from this equilibrium

because we use the pH of the bulk fog water.[31] Following Guo et al.,[26] the fraction of available NH$_3$ that partitions to the fog water at equilibrium, ε_{NH_4}, is given by

$$\varepsilon_{NH_4} = \frac{H_{NH_3}^* RT \text{ LWC}_f}{1 + H_{NH_3}^* RT \text{ LWC}_f} \tag{3}$$

where T is the measured temperature in K, LWC$_f$ is the measured liquid water content of the air in g m^{-3}, R (=0.082 atm L mol^{-1} K^{-1}) is the ideal-gas constant, and $H_{NH_3}^*$ is the effective Henry's law constant calculated at the measured fog water pH

$$H_{NH_3}^* = H_{NH_3} \frac{K_{a_1}}{K_w} [H^+] \tag{4}$$

where H_{NH_3} (=62 M atm^{-1}) is the Henry law constant for NH$_3$ at 298 K, $K_{a_1} = 1.7 \times 10^{-5}$ M, and $[H^+]$ is the hydronium ion concentration in the fog water.

Given that the fog water pH and concentration of ammonium and liquid water are known, eqs 3 and 4 can be combined to give NH$_{3(fog)}^{eq}$

$$\text{NH}_{3(fog)}^{eq} = \frac{\text{NH}_{4(fog)}^+}{H_{NH_3} \frac{K_{a_1}}{K_w} RT [H^+] \text{ LWC}_f} \tag{5}$$

where NH$_{3(fog)}^{eq}$ is the equilibrium concentration of ammonia in the fog, and NH$_{4(fog)}^+$ is the ammonium concentration of the fog water.

Ricci et al.,[32] investigating the uptake of soluble gases by fog droplets, showed that deviations from bulk equilibrium can occur and thus should be accounted for, at least approximately. For this, we define an equilibrium deviation ratio, $D_r = \text{NH}_{3(fog)}/\text{NH}_{3(fog)}^{eq}$, as the ratio between the estimated (NH$_{3(fog)}$) and bulk equilibrium gas-phase ammonia concentration. If D_r is constrained from observations, it can then be used together with eq 5 to provide the estimated concentration of ammonia in the fog

$$\text{NH}_{3(fog)} = \left[\frac{D_r K_w}{H_{NH_3} K_{a_1} RT} \right] \frac{\text{NH}_{4(fog)}^+}{[H^+] \text{ LWC}_f} \tag{6}$$

Given that our analysis refers to the bulk composition of fog water (in which we cannot keep track of the size and pH of the single droplets), actually, the deviation ratio (D_r) can change depending on the duration and characteristics of the fog event (as already hypothesized and empirically measured by Pandis and Seinfeld[31] and by Ricci et al.[32]), and especially, depending on the pH of the fog water solution. Pandis and Seinfeld[31] proved that for all fogs the difference in pH among droplets of different sizes (larger droplets tend to be more alkaline as they form on alkaline dust particles), even if the system is in equilibrium, leads to supersaturation of the bulk aqueous phase compared to the gas phase. To account for this effect too, using the available measured data (referring to the last 2 years analyzed, 2017−2018), we estimate (following the steps described in the Supporting Information, Section S1) the possible range of D_r values due to different fog events (Figure S1) and we explicitly determine the relationship between D_r and the measured fog-pH for the 25-year dataset (Figure S2).

We tested consequently different D_r values in the range suggested by our analysis as well as the uncorrected estimation

(i.e., $D_r = 1$) corresponding to the equilibrium (Supporting Information, Section S1). In particular, we compare the performance of the different D_r estimations in terms of the agreement between (a) simulated and observed ammonia/ammonium concentrations at SPC and (b) estimated $NH_{3(fog)}$ concentrations and $NH_{3(g)}$ measurements available also in other places of the Po Valley, like Lombardy (where $NH_{3(g)}$ is measured since 2003).

The results of this comparison suggest that D_r expressed as a function of fog-pH is more appropriate, as it corresponds and correlates well with the available parallel $PM_{2.5}$ and $NH_{3(g)}$ measurements at SPC (Figure S3) and leads to the estimated $NH_{3(fog)}$ concentrations, which are comparable with other Po Valley background sites (Figure S4).

4. RESULTS AND DISCUSSION

4.1. Model Evaluation. The ability of the thermodynamic analysis of fog water composition to estimate aerosol pH is tested first for a subset of data collected from August 2017 to October 2018 focusing on ammonia partitioning. For this period, measurements of both fog and $PM_{2.5}$ compositions as well as $NH_3(g)$ concentrations are available. ISORROPIA-II was used to simulate the partitioning in the system using the fog composition and the estimated $NH_{4(fog)}^+ + NH_{3(fog)}$ as inputs for the total ammonia. These predictions are then compared against the measurements of $PM_{2.5}$ NH_4^+ and $NH_3(g)$ concentrations.

The predictions of ISORROPIA-II for the ammonia/ammonium concentrations obtained from the fog water composition and the estimated NH_3 inside the fog are quite consistent with those using the measured $NH_3(g)$ and $PM_{2.5}$ aerosol composition (Figure 1) as inputs. The differences in
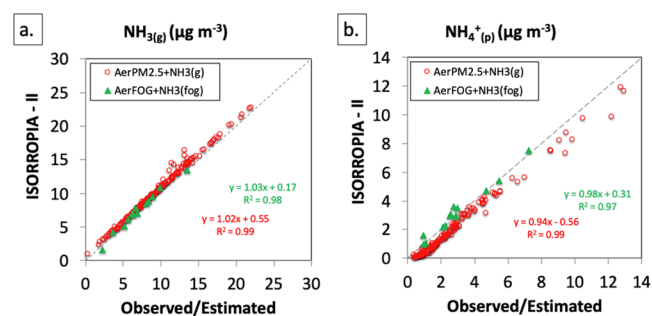

Figure 1. Evaluation of the ISORROPIA-II ammonia/ammonium concentrations: simulated concentrations of ammonia (a) and ammonium (b) are plotted against the corresponding observed/estimated values. Red markers refer to the measured $NH_3(g)$ and $PM_{2.5}$ aerosol composition; green markers represent the partitioning obtained from the fog water composition and the estimated NH_3 inside the fog.

concentrations are, on average, $-1 \pm 3\%$ for the gas-phase ammonia and $8 \pm 3\%$ for the particulate ammonium (Figure S2). The two approaches also result in consistent pH values with an average difference of 0.06 ± 0.27 pH units (Figure 2).

Moreover, a direct comparison of the fog water and $PM_{2.5}$ composition for all of the parallel available samples (63 samples spanning from 2011 up to 2018) is also reported in Table S1 and Figure S6, and shows a general agreement. This confirms that the fog water thermodynamic analysis provides a consistent alternative for predicting the pH in the ambient aerosol with reasonable accuracy.

If we do not include the observed gas-phase NH_3, the predicted pH decreases by 1.01 ± 0.12 units using $PM_{2.5}$ composition (Figure 2). This difference (hereinafter, defined as ΔpH AerPM) is consistent with the findings of previous studies[6,8,33] that neglect considering the gas-phase NH_3 when inferring aerosol pH. The difference of the fog-water-based pH predictions (AerFOG pH) with and without the estimated gas-phase ammonia (ΔpH AerFOG) is slightly higher at 1.09 ± 0.34, respectively (Figure 2). The calculation of ammonia concentration from the fog water composition is unambiguous and leads to considerably improved pH estimates.

4.2. Aerosol pH Trend in the Last 25 Years. The aerosol pH was estimated using the proposed approach based on the 577 fog water samples collected at SPC over the last 25 years. To investigate typical conditions, the daily mean values of RH and T (calculated as the average of the 24 h of each corresponding day) were used for the ISORROPIA-II calculations, considering them as the best approximation of the average conditions that particles were exposed to before the onset of fog.

The trend of the estimated aerosol pH over the last 25 years is shown in Figure 3. We used annual averages to help to ensure that errors are independent and identically distributed, as suggested by Hess et al.[34] The variability of the aerosol pH during each year is considerable. In 1997, for instance, the calculated pH ranged from 1.38 to 5.51. The variability among years is also remarkable with the highest annual average of 5.18 in 1993 and the lowest of 3.66 in 2010. Given this high variability, the general trend of the aerosol pH over time is identified by applying an interquartile-range rule to remove the extreme values from the annual averages (see the Supporting Information, Section S3), and we obtain a net pH decreasing trend for the whole period 1993−2018 at a 99% confidence interval (Figures 3, S7, and S8). The calculated means from applying the interquartile-range rule show that during 1993−2002, the average aerosol pH was 4.62 (with the highest annual average of 5.18 in 1993) while from 2003−2012 it was 4.53 (with the highest value of 5.10 in 2004) dropping to an average value of 4.27 over the 6 years between 2013 and 2018 (with a maximum value of 4.31 in 2016).

Given the importance of the gas-phase ammonia concentration inside the fog layer, $NH_{3(fog)}$, in the determination of the aerosol pH trend over time, an additional evaluation of the pH variability due to different possible estimations of the gaseous ammonia concentrations is shown in the Supporting Information (Sections S4 and S5, Figures S9−S11). All tests confirm the decreasing trend of the aerosol pH based on the fog composition (AerFOG pH) within a limited range of variability depending on the chosen gaseous ammonia estimation. Aerosol acidity has increased by approximately 0.5−1 pH units over the examined 25-year period.

The fog water pH is also shown in Figure 3, which shows an increasing trend at a 99% confidence interval (using least-squares regression). Giulianelli et al.[16] had already analyzed this increasing trend of the fog pH at SPC and related it to the decreasing concentrations of the major acidic species NO_3^- and SO_4^{2-} (Figure S12). SO_2 and NO_x emissions have been reduced in Italy but also throughout Europe—without a concurrent decrease in the fog water content during episodes. This behavior is consistent with other European and American datasets (see Pye et al.[2] and references therein).

These different trends, although counterintuitive at first glance, are consistent with the thermodynamics of the fog and
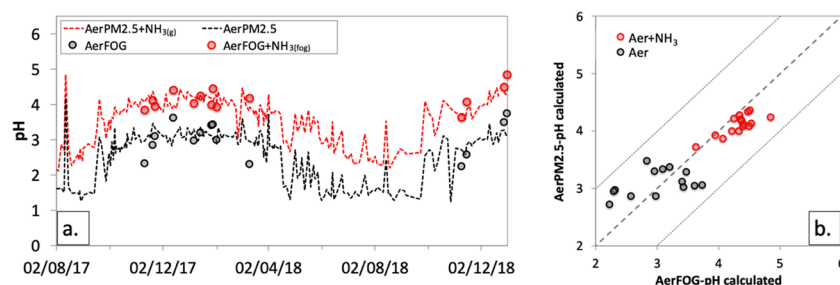
Figure 2. pH values calculated using ISORROPIA-II from the PM$_{2.5}$ composition (AerPM2.5 pH) and from the fog water composition (AerFOG pH). (a) Time series of AerPM2.5 (dashed lines) and AerFOG pH (markers) for the evaluation dataset. (b) The pH values of AerPM2.5 (y-axis) and AerFOG (x-axis) for parallel samples. The dashed lines indicate ΔpH = 1, 0, and −1. In both panels, black line and markers represent the calculation made without gaseous ammonia (NH$_{3(g)}$) as input, while red line and markers represent the results using particle/fog NH$_{4(p)}^+$ + gaseous ammonia measured (NH$_{3(g)}$) or estimated by fog composition (NH$_{3(fog)}$), respectively.
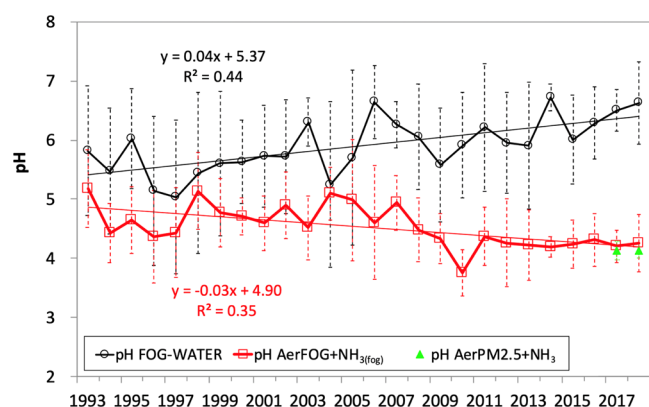

Figure 3. Fog and aerosol pH trends as measured directly in fog water or calculated using ISORROPIA-II. Black circles are the annual average of the pH measured; red squares are the annual average values of the aerosol pH calculated using ISORROPIA-II starting from the fog ionic composition with the gaseous estimated NH$_{3(fog)}$ as input (pH AerFOG + NH$_{3(fog)}$). Green triangles are the annual average values of the aerosol pH calculated using ISORROPIA-II starting from PM$_{2.5}$ ionic composition with the measured gaseous NH$_3$ as input (pH AerPM2.5 + NH$_{3(g)}$). Error bars represent the standard deviations of the measured/calculated pH values.

aerosol systems. The water concentration in the fog is not driven by the amount of aerosol but rather only by the meteorological conditions, especially the cooling rate when fog is being formed. In contrast, the aerosol liquid water scales with the amount of aerosol. As a result, the aerosol pH tends to change much less with the aerosol amount (because liquid water changes accordingly).[1,10] At the same time, there is the potential for a small decrease in the pH with reduced aerosol because relatively larger amounts of ammonium need to volatilize to establish equilibrium between the gas and particulate phases.[1] As this ammonium leaves the particles, the main cation that neutralizes the acids is depleted. This means that the aerosol pH tends to become more acidic even if the strong acidic components (sulfate and nitrate formed from SO$_2$ and NO$_x$) are reduced. Another factor that can reduce aerosol pH is the change of meteorological parameters (RH and T) observed at SPC over the 25-year period (Figure S13). The role of the different drivers of the observed trends will be discussed in a subsequent section.

4.3. Effect of RH and T Variability on pH Predictions. In our analysis, as already mentioned, we considered daily mean values of relative humidity and temperature as the best approximation of the conditions that particles were exposed to

before the onset of fog. To understand how predicted aerosol pH varies throughout each day depending on the RH and T, we repeat the simulation using the RH and T continuously measured during the fog-events and averaged over the fog-sampling time periods, which possibly represents the atmospheric conditions closest to the fog-scavenging.

The resulting pH also shows a decreasing annual average trend (Figure S14), with a reduction of ∼1.5 pH units over the 25-year period. The difference between the two trends is indicative of the effect of the diurnal variability in meteorology on the predicted aerosol pH. Taking these differences into account, we can state that the aerosol pH has decreased by 0.5−1.5 units over the last 25 years.

The different slope of the two pH trends in Figure S14 indicates the important role of RH in determining the aerosol pH by influencing the aerosol liquid water content. To further investigate this effect, we used a constant RH value equal to 99, 95, 90, 85, 80, 75, and 70% and repeated the pH calculation. The aerosol pH values calculated using RH = 99% are systematically higher than all the others (Figure S15). For lower values of the RH, the trend becomes weaker, highlighting the importance of RH in pH determination at least in a region such as Po Valley, characterized by high RH.

4.4. Drivers of Aerosol pH Reduction. To understand the drivers of the observed aerosol pH reduction, we apply a multiple linear regression analysis on the simulated aerosol pH, following the approach of Rosenfeld et al.[35] A first regression is applied to the aerosol pH with all of the independent variables (ionic composition and meteorological parameters) used by ISORROPIA-II to calculate the total R^2. The regression is then repeated, sequentially omitting one variable at a time to retrieve the contribution of each individual variable to the total variance explained (or R^2). The strongest contribution is by the total ammonium (NH$_4^{TOT}$, i.e., gas plus particle phase), representing, alone, 35% of the total variance explained, followed by sulfate (SO$_4^{2-}$) and RH contributing 17 and 16% each, respectively, and calcium (Ca^{2+}) contributing 11% (Table S2). Grouping the variables by category, we find that the major ions (NH$_4^{TOT}$, NO$_3^-$, SO$_4^{2-}$, and Cl$^-$) are responsible for 61% of the variability, the meteorological parameters (RH and T) for another 23%, and the nonvolatile cations (K$^+$, Na$^+$, Ca^{2+}, Mg^{2+}) for the remaining 16%.

These findings confirm the importance of the aerosol chemical composition changes over the years, but point out the important contribution of decreasing RH and increasing T already observed at SPC (Figure S13) in determining the pH trend. This influence should be accounted for when

considering future climate change and its interaction with air quality.

4.5. Relationship between Wintertime/Fog-Related pH and Other Seasons. Our analysis shows a decreasing trend in aerosol pH based on the fog water chemical composition. However, the fog composition is representative only of the period between November and March when fog events actually occur, and in particular only of the days in which fog occurs. Nevertheless, based on the pH sensitivity to RH (Figure S15) and on the difference between the average RH during foggy days and during all winter (Table S3), we can expect a change in pH estimation of about 0.2−0.3 units due to the variability of RH in wintertime (which never drops below 80% on a seasonal average basis). Regarding seasons without fog events, the 7 years (2011−2018) of available aerosol data[24] allow a robust characterization of the SPC aerosol pH seasonality over the recent past. The strong seasonality of aerosol pH (calculated using the monthly average of the available gaseous ammonia measurements for constraining the model, as described in the Supporting Information, Section S9, Figure S16) is recognizable, with the highest average values of 4.19 during winter (in good agreement with the pH calculated from fog composition in the same period 2011−2018) and the lowest of 2.61 during summer (Figure S17). The variation of more than 1.5 pH units between winter and summer can be the result of the seasonal changes in meteorological conditions (mean wintertime temperature and RH are 276 K and 85%, while the summertime ones are 297 K and 62%, respectively) but also of the changing emissions like biomass burning in the wintertime, agricultural activities and photochemical processes during summer.[36] These seasonal ranges are consistent with the seasonality reported in other locations (e.g., Pye et al.,[2] and references therein).

5. IMPLICATIONS

Information on aerosol pH trends over time is limited in Europe as well as around the world, owing to the scarcity of relevant data. Long-term monitoring programs for cloud/fog composition and acidity are also limited, but there are locations around the world where such measurements have been made routinely, or at least periodically, over periods of a decade or more. Our analysis suggests a novel way to calculate the pre-fog aerosol pH using fog compositional data in a thermodynamically consistent way, which can be useful to evaluate long-term trend of particle acidity also in other regions of the world for which data are available (e.g., Central Valley in CA; Whiteface mountain, NY; etc.[2]).

The Po Valley dataset used in this work shows an increasing trend of the fog water pH.[16] We show for the first time that this increasing pH of cloud/fog water may not be indicative of the trend in aerosol acidity. In the case of the Po Valley, the fog and the aerosol have opposite trends during the last 25 years. We demonstrate that this aerosol pH reduction trend is thermodynamically robust and it is driven by the contemporary decrease of the corresponding air pollutants due to the environmental policies and by the changing meteorological parameters (RH and T), possibly a result of regional climate change. The Po Valley is dominated by ammonia emissions and its aerosol is characterized by pH and liquid water content levels similar to those in E. Asia during haze episodes.[26]

The Po Valley is a well-known air quality hotspot characterized by particulate matter (PM) levels well above the limit set by the European Air Quality Directive and by the

World Health Organization. These high concentrations are dominated during the cold season (almost half of the year) by ammonium nitrate (which during winter represents 26−43% of total $PM_{2.5}$ mass[20]). Given their semivolatility and their acid−base activity, nitrate, and ammonium are the aerosol species most sensitive to pH. Nenes et al.[37] developed a new conceptual framework explicitly considering pH, aerosol liquid water content, and temperature as the main parameters controlling secondary inorganic PM sensitivity. Figure 4 places
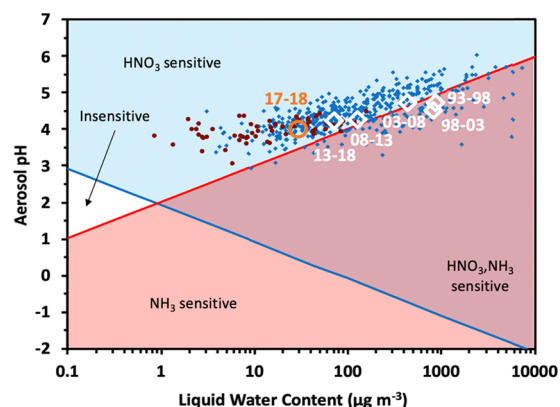

Figure 4. Distribution of aerosol pH versus aerosol liquid water content from both fog composition (blue points) and $PM_{2.5}$ composition (brown points) inside the chemical domains of aerosol sensitivity to NH_3 and NO_x emissions as introduced by Nenes et al.[37] The blue line defines the characteristic pH when the aerosol is sensitive to changes in the available nitrate and the red line in ammonia. These are calculated for the average temperature of the winter periods (280 K). $PM_{2.5}$ data are for 2017−2018 wintertime samples for which both $NH^+_{4(p)}$ and $NH_{3(g)}$ measurements are available. Bigger markers indicate the average values of the corresponding multiyear period reported below each of them: white symbols refer to calculations based on the fog water data and the orange circles refer to the aerosol and gas-phase ammonia data.

the Po Valley aerosol pH (both based on fog and aerosol data) in this framework. Based on this, the SPC area from November to March (fog season) is in the regime in which aerosol nitrate formation is highly efficient. This is true for the aerosol pH calculated both by fog water (i.e., referring to foggy days) and by $PM_{2.5}$ composition (i.e., including both foggy and non-foggy wintertime days of 2017−2018).

Considering the definitions of Nenes et al.[37] and the average values of temperature and aerosol liquid water content corresponding to the $PM_{2.5}$ samples collected at SPC during the cold season (280 K and 28.8 μg m^{-3}, respectively), we calculate the threshold for the change of acidity regime to be at a pH of ∼0.5. This pH value is well below the lowest observed pH values (3.76 as an annual average for 2010). However, if the decreasing trend of aerosol pH continues in the future and the pH drops to the threshold level, aerosol nitrate will remain almost exclusively in the gas phase as HNO_3, regardless of the amount present. If and when this change happens depends on the rate of future reduction in emissions of NH_3 and NO_x (precursors of aerosol ammonium and nitrate) and on the changes of T and RH. Increasing T and decreasing RH will tend to shift the threshold to higher pH values as the effect of the liquid water content decreases. For the time being, the wintertime composition has been gradually moving along the years from the top right (HNO_3/NH_3-sensitive regimes) toward the top left side of the graph (HNO_3-sensitive regime)

(Figure 4), mostly because the aerosol liquid water content, in particular, has decreased significantly due to changes in PM concentrations and also to decreasing RH (Figure S13). pH has seen less of a drop because of these changes.

Currently, the PM sensitivity regime remains in the HNO_3-sensitive area throughout the year, with a tendency however to be close to the NH_3-sensitive regime during summer (Figure 5). This seasonality of the PM sensitivity in the Po Valley is
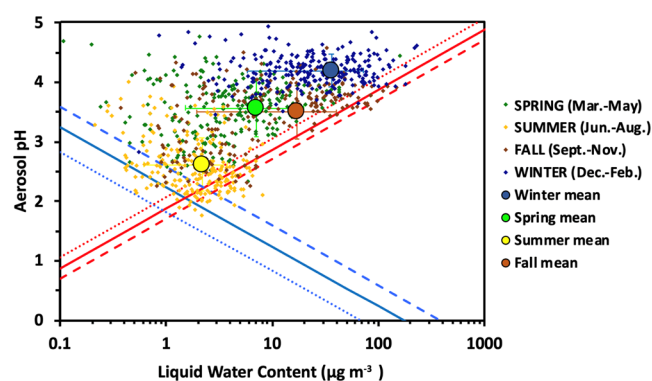

Figure 5. Seasonality of the distribution of aerosol pH versus liquid water content inside the chemical domains of aerosol sensitivity introduced by Nenes et al.[37] Characteristic pH for defining when the aerosol is sensitive to changes in the available nitrate (blue lines) and ammonia (red lines) are calculated for the annual average temperature (=287 K, solid lines) ± its standard deviation (=295 K, dotted lines, and =278 K, dashed lines, respectively).

important for effective pollution control policies. This means that, currently, NO_x controls would be most effective for $PM_{2.5}$ reduction in the Po Valley both during summer and winter. In the future, however, seasonal transitions to the NH_3-sensitive region may occur, meaning that the NH_3 reduction policy may become increasingly necessary. Future work will focus on the implications of the emission and meteorological trends for the deposition of reactive nitrogen.[38]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.1c00651.

> Deeper descriptions of the modeling methods (e.g., estimation of gaseous ammonia from fog water composition; NH_3 estimation effect on the aerosol pH variability and RH sensitivity test); statistical analysis of the pH trend; details on the trends of pollutants and meteorological parameters; details on the results of the multiple linear regression analysis to study the drivers of aerosol pH reduction (PDF)

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Author Contributions

M.P. and A.N. developed the acidity inference method and designed the research; S.D., L.T., S.F., and M.C.F. managed the fog-sampling campaigns; M.P., S.D., S.G., M.R., and F.M. contributed to the chemical analyses; D.B. and A.T. performed aerosol sampling and ammonia measurements; M.P., A.N., S.N.P., and S.D. wrote the paper; S.N.P., M.R., S.F., M.C.F., S.G., and S.D. contributed to the scientific discussion and paper correction. All authors have given approval to the final version of the manuscript.

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