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 are not available for long periods of time. Fogs composition datasets 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 available gas-particle composition data. Applying the new method to historical (25 year) 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. Observed fog water pH also increased 1 unit over the same period. Analysis of the simulated aerosol pH reveals that the aerosol acidity trend is driven by decreases of aerosol precursor concentrations, and changes in temperature and relative humidity. Currently, NOx 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 NH$_3$ reduction policy may become increasingly necessary.

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, human and ecosystems health and climate. Despite its importance, the direct measurement of the pH of atmospheric aerosol is highly challenging, with only few available
techniques for its determination. 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. The most reliable estimates of aerosol acidity to date are obtained through thermodynamic analysis of ambient observations. In this approach, aerosol thermodynamic models (such as ISORROPIA-II) are applied to observations of concentrations of species in the gas and aerosol phase that control the water uptake of the aerosol. If the observed gas-particle partitioning of species sensitive to aerosol pH (e.g., \( \text{NH}_3/\text{NH}_4^+ \), \( \text{HNO}_3/\text{NO}_3^- \)) 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.

Using thermodynamic analysis, datasets of aerosol acidity are appearing with increasing frequency (see the review by Pye et al.), however their number and temporal span is limited compared to the large number of PM composition datasets available, because the required concurrent measurements of the gas-phase concentrations of \( \text{NH}_3 \) and/or \( \text{HNO}_3 \) is often unavailable. In most cases, even if it may not be the case for dust or sea salt particles, \( \text{NH}_3 \) concentration is enough to derive aerosol acidity, as it acts as a buffer that controls aerosol pH. In the absence of \( \text{NH}_3 \) data, one can still obtain robust pH estimates if \( \text{NO}_3^-/\text{HNO}_3 \) observations are available. If neither \( \text{HNO}_3 \) or \( \text{NH}_3 \) observations are available, the pH estimates can still be obtained, albeit with a constrained (but non-negligible) bias.

To date, thermodynamic analysis has been applied exclusively to aerosol–gas phase composition data. This approach is the most straightforward, as it provides the direct input required by thermodynamic models to calculate semi-volatile partitioning and aerosol pH. Other non-conventional datasets, however, may provide aerosol pH with an appropriately formulated thermodynamic analysis. Fog water data offer such a potential, as fogs – which act like natural
“mist chamber” samplers - tend to scavenge significant fractions of aerosol mass and soluble vapors such as NH₃, HNO₃ 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. Fog water pH and liquid water content can also be directly measured, allowing for estimations of gas-phase aerosol precursors (the main ones being NH₃, HNO₃ and HCl¹⁴). 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 production of secondary organic aerosol, especially during intense haze events¹⁵.

In this study, we evaluate the potential of using fog water ionic composition data to estimate the pH of the preexisting aerosol. The method is evaluated using data collected in the Po Valley of Italy. Concurrent measurements of aerosol and gas phase composition, before fog events are also used to estimate 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 years¹². 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., SO₂, NOₓ and NH₃) and meteorological parameters (T and RH) are explored.

2. Experimental methods

2.1. Fog water collection and analysis

Fog water has been 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 1980's\textsuperscript{17,18,19,20}. Fog water is sampled using an automated active string collector extensively described by Fuzzi et al.\textsuperscript{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 air flow 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, measures the liquid water content of the fog (LWC) with a time resolution of 1 min. This monitor is used to activate the string collector when LWC exceeds 0.08 g m$^{-3}$. This threshold corresponds to a visibility of approximately 200 m\textsuperscript{22} and the fog is considered dense (the meteorological definition of fog is visibility less than 1 km).

Direct pH measurements are carried out in the liquid fog samples with a Crison micropH 2002 pH meter: this measure is taken in the laboratory of ISAC-CNR (at Bologna, about 40 Km far from SPC) as soon as the sample arrive from the field. Usually it happens after a short trip by car (30-40 min. of transport). If for any reasons the time is longer, the fog sample is kept refrigerated in fridge or directly outside (closed in the corked sampling bottle, on the terrace of the laboratory) for at least 60 minutes in order 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\textsuperscript{23}. The results of this chemical characterization and the temporal trends in the observed chemical and physical parameters have been presented by Giulianelli et
As reported in Giulianelli et al.\textsuperscript{16}, analytical problems affected chromatographic data from 1989/90 to 1992/93 and these samples are 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. \textit{PM}_{2.5} and ammonia measurements

Daily \textit{PM}_{2.5} and gaseous ammonia (NH\textsubscript{3}) measurements were made by the Regional Agency for prevention, environment and energy (ARPAE) of Emilia-Romagna, Italy. The \textit{PM}_{2.5} filter sampling started in the framework of the Supersito project (www.arpae.it/supersito) from November 2011 and continues until today following the protocol described by Ricciardelli et al.\textsuperscript{24}. \textit{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\textsubscript{4}\textsuperscript{+}, Na\textsuperscript{+}, K\textsuperscript{+}, Ca\textsuperscript{2+}, Mg\textsuperscript{2+}, Cl\textsuperscript{-}, NO\textsubscript{3}\textsuperscript{-}, SO\textsubscript{4}\textsuperscript{2-}). After the collection with a Single Channel Monitor (SWAM FAI Rome, Italy) operating at the standard flowrate of 38.3 L min\textsuperscript{-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, USA). Gaseous ammonia (NH\textsubscript{3}) hourly measurements are available at SPC starting from August 2017 thanks to a chemiluminescence ammonia analyzer (Model 201E, Teledyne-API, San Diego CA, USA) 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 (simp.arpaie.it/dext3r/). T and RH measurements are validated against 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) calculates the composition and phase state of a \(\text{K}^+\text{–Ca}^{2+}\text{–Mg}^{2+}\text{–NH}_4^+\text{–Na}^+\text{–SO}_4^{2-}\text{–NO}_3^-\text{–Cl}^-\text{–water}\) 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\(^1,8,12,25,26,27\).

Similar to previous studies, the definition of pH used here is:

\[
pH = -\log_{10} \gamma_{H^+} H_{aq}^+ = -\log_{10} \frac{1000 \gamma_{H^+} H_{aq}^+}{W_i + W_o} \equiv -\log_{10} \frac{1000 \gamma_{H^+} H_{air}^+}{W_i} \tag{1}
\]

where \(\gamma_{H^+}\) is the hydronium ion activity coefficient (here assumed unity), \(H_{aq}^+\) (mol L\(^{-1}\)) is the hydronium ion concentration in the aerosol aqueous phase, \(H_{air}^+\) (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 organic species and their overall effect on water activity and pH. Guo et al.\(^8\), Song et al.\(^7\), Vasilakos et al.\(^28\), and Battaglia Jr. et al.\(^29\) evaluated this assumption and found organics to have a secondary effect on aerosol pH, somewhere between 0.15 and 0.3 pH units. So, since the organic
We used ISORROPIA-II in the partitioning (“forward”) mode for metastable aerosol. In this configuration, the model calculates the equilibrium partitioning given the total concentration (gas plus particles) of various species together with RH and T as input. Considering that fog scavenging efficiency of inorganic species are generally larger than 70% and show little variability\textsuperscript{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 ($C_{i,\text{air}}, \mu g m^{-3}$) is obtained by multiplying their concentration in fog water ($C_{i,\text{fog}}, \mu g mL^{-1}$) with the liquid water content of the fog ($LWC_{\text{air}}, mL m^{-3}$):

$$C_{i,\text{air}} = C_{i,\text{fog}} LWC_{\text{f}}$$ \hspace{1cm} (2)

Given the relatively high pH of the fog water some ammonia is 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 (2). A similar inference of gas-phase HNO$_3$ and HCl is deemed unnecessary in this case, given the high value of pH and $LWC_{\text{f}}$ of fogs in SPC\textsuperscript{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 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\textsuperscript{6}. 

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 $W_i$. 

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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 quasi-equilibrium 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 fog water NH$_4^+$, and then correct to account for any apparent departure from this equilibrium because we use the bulk fog water pH$^{31}$. Following Guo et al.$^{26}$, the fraction of available NH$_3$ that partitions to the fog water at equilibrium, $\varepsilon_{NH4}$, is given by:

$$
\varepsilon_{NH4} = \frac{H_{NH3}^* RT LWC_f}{1 + H_{NH3}^* RT LWC_f} \tag{3}
$$

where $T$ is the measured temperature in K, $LWC_f$ is the measured liquid water content of the air in g m$^{-3}$, $R$ is the ideal-gas constant equal to 0.082 atm L mol$^{-1}$K$^{-1}$, and $H_{NH3}^*$ is the effective Henry’s law constant calculated at the measured fog water pH:

$$
H_{NH3}^* = H_{NH3} \frac{K_{a1}}{K_w} [H^+] \tag{4}
$$

where $H_{NH3}$ is the Henry law constant for NH$_3$ equal to 62 M atm$^{-1}$ at 298 K, $K_{a1} = 1.7 \times 10^{-5}$ 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, equations (3) and (4) can be combined to give $NH_{3}^{eq}(fog)$:

$$
NH_{3}^{eq}(fog) = \frac{NH_4^+(fog)}{H_{NH3} \frac{K_{a1}}{K_w} RT[H^+] LWC_f} \tag{5}
$$
where \( NH_{3(\text{fog})}^{eq} \) is the equilibrium concentration of ammonia in the fog, and \( NH_{4(\text{fog})}^{+} \) is the fog water ammonium concentration.

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

\[
NH_{3(\text{fog})} = \left[ \frac{D_r K_w}{K_{HNH_{3}K_{a1RT}}} \right] \frac{NH_{4(\text{fog})}^{+}}{[H^+] LWC_f} \tag{6}
\]

Given that our analysis refers to the bulk composition of fog-water (in which we cannot keep track of 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\textsuperscript{31} and by Ricci at al.\textsuperscript{32}) and especially depending on the pH of the fogwater solution. Pandis and Seinfeld\textsuperscript{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 a supersaturation of the bulk aqueous phase compared to the gas phase. In order to account for this effect too, using the available measured data (referring to the last 2 years analyzed, 2017-18), we estimate (following the steps described in the Supplementary 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-years dataset (Figure S2).
We tested consequently different $D_r$ in the range suggested by our analysis as well as the uncorrected estimation (i.e., $D_r = 1$) corresponding to the equilibrium (Supplementary Section S1). In particular, we compare the performance of the different $D_r$ estimations in term 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 suggests that $D_r$ expressed as 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 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. In this period measurements of both fog and PM$_{2.5}$ compositions are available as well as NH$_3$(g) concentrations. 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 estimated NH$_3$ inside the fog are quite consistent with those using as inputs the measured NH$_3$(g) and PM$_{2.5}$ aerosol composition (Figure 1). The differences in concentrations are on average -1±3% for gas-phase ammonia and 8±3% for 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 the parallel available samples (63 samples spanning from 2011 up to 2018) is also reported in Table S1 and Figure S6 showing 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 findings of previous studies$^{6,8,33}$ that neglect consideration of 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 the 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. In order to investigate typical conditions, the daily mean values of RH and T (calculated as average of the 24h 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 time trend of estimated aerosol pH over the last 25 years is showed in Figure 3. We used annual averages to help ensure that errors are independent and identically distributed, as suggested
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 Supplementary Section S3), and we obtain a net pH decreasing trend for the whole period 1993-2018 at a 99% confidence interval (Figure 3 and Figures S7-S8). The calculated means from applying the interquartile-range rule show that during 1993-2002, 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 in the Supplement (sections S4 and S5, Figure 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 and it shows an increasing trend at a 99% confidence interval (using least squares regression). Giulianelli et al.\textsuperscript{16} already analyzed this increasing trend of 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 fog water content during episodes. This
behavior is consistent with other European and American datasets (Pye et al.\textsuperscript{2} and references therein).

These different trends, although counterintuitive at first glance, are consistent with the thermodynamics of the fog and 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 forming. In contrast, aerosol liquid water scales with the amount of aerosol. As a result, aerosol pH tends to change much less with aerosol amount (because liquid water changes accordingly)\textsuperscript{1,10}. At the same time, there is the potential for a small decrease in pH with reduced aerosol, because relatively larger amounts of ammonium need to volatilize to establish equilibrium between the gas and particulate phases\textsuperscript{1}. As this ammonium leaves the particles, the main cation that neutralizes the acids is depleted. This means that aerosol pH tends to become more acidic even if the strong acidic components (sulfate and nitrate formed from SO2 and NOx) are reduced.

Another factor that can reduce aerosol pH is the change of meteorological parameters (RH and T) observed at SPC along the 25-years period (Figure S13). The role of the different drivers of the observed trends will be discussed in a subsequent section.

4.3 RH and T variability effect 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 represent the atmospheric conditions most close 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 declined 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 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 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.\(^3\). A first regression is applied to the aerosol pH with all the independent variables (ions composition and meteorological parameters) used by ISORROPIA-II in order to calculate the total \(R^2\). The regression is then repeated, sequentially omitting a 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 (\(\text{NH}_4^{\text{TOT}}\), i.e., gas plus particle-phase), representing alone 35% of the total variance explained, followed by sulfate (\(\text{SO}_4^{2-}\)) and RH contributing 17 and 16% each respectively, and calcium (\(\text{Ca}^{2+}\)) contributing 11% (Table S2). Grouping the variables by category we find that
the major ions ($\text{NH}_4^{\text{TOT}}$, $\text{NO}_3^-$, $\text{SO}_4^{2-}$ and $\text{Cl}^-$) are responsible for 61% of the variability, the meteorological parameters (RH and T) for another 23%, and the non-volatile cations ($\text{K}^+$, $\text{Na}^+$, $\text{Ca}^{2+}$, $\text{Mg}^{2+}$) for the remaining 16%.

These findings confirm the importance of the aerosol chemical composition changes along 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, allow a robust characterization of the SPC aerosol pH seasonality over the recent past. A strong seasonality of aerosol pH (calculated using monthly average of the available gaseous ammonia measurements for constraining the model, as described in Supplementary 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. These seasonal ranges are consistent with the seasonality reported in other locations (e.g., Pye et al., 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 pre-fog aerosol pH using fog compositional data in a thermodynamically consistent way, which can be useful to evaluate long-term trend of particles acidity also in other region of the world for which data are available (e.g., Central Valley in CA; Whiteface mountain, NY; etc.).

The Po Valley dataset used in this work shows an increasing trend of fog water pH. 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\textsuperscript{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 \(\text{PM}_{2.5}\) mass\textsuperscript{20}). Given their semi-volatility and their acid-base activity, nitrate and ammonium are the aerosol species most sensitive to pH. Nenes et al.\textsuperscript{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 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 \(\text{PM}_{2.5}\) composition (i.e., including both foggy and non-foggy wintertime days of 2017-18).

Considering the definitions of Nenes et al.\textsuperscript{37} and the average values of temperature and aerosol liquid water content corresponding to the \(\text{PM}_{2.5}\) samples collected at SPC during the cold season (280 K and 28.8 $\mu$g 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 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 $\text{HNO}_3$, regardless of the amount present. If and when this change will happen depends on the rate of future reduction in emissions of $\text{NH}_3$ and $\text{NO}_x$ (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
winter-time composition has been gradually moving along the years from the top right
(HNO$_3$/NH$_3$-sensitive regimes) toward 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 Po Valley is important for effective pollution control
policies. This means that currently, NOx 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 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 on the ACS
Publications website. Deeper descriptions of the modeling methods (e.g., estimation of gaseous
ammonia from fog-water composition, NH$_3$ estimation effect on 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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Notes

The authors declare no competing financial interest.

Author Contributions

MP, and AN developed the acidity inference method and designed the research; SD, LT, SF, and MCF managed the fog-sampling campaigns; MP, SD, SG, MR, and FM contributed to the chemical analyses; DB, and AT performed aerosol sampling and ammonia measurements; MP, AN, SP, and SD wrote the paper; SP, MR, SF, MCF, SG, and SD contributed the scientific discussion and paper correction. All authors have given approval to the final version of the manuscript.

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**Figure 1.** Evaluation of the ISORROPIA-II ammonia/ammonium concentrations: simulated concentrations of ammonia (panel a) and ammonium (panel b) are plotted in y-axes against the corresponding observed/estimated values (x-axes). 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 estimated NH$_3$ inside the fog. Dashed line shown is the 1 : 1 for comparison.
**Figure 2.** pH calculated by ISORROPIA-II from PM2.5 composition (AerPM2.5 pH) and from fog-water composition (AerFOG pH). Panel a: time series of AerPM2.5 (dashed lines) and AerFOG pH (markers) for the evaluation dataset. Panel b: AerPM2.5 (y-axis) and AerFOG (x-axis) pH values for parallel samples. The dashed lines indicate delta pH = 1, 0, and -1. In both the panels, black line and markers represent the calculation made without gaseous ammonia (NH$_3$(g)) as input, while red line and markers represent the result 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 into fog-water or calculated by ISORROPIA-II. Black circles are the annual average of the pH measured; red squares are the annual average values of aerosol pH calculated by 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 aerosol pH calculated by ISORROPIA-II starting from PM2.5 ionic composition with the measured gaseous NH$_3$ as input (pH AerPM2.5+NH$_3$). Error bars represent the standard deviations of the measured/calculated pH values.
**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. (2020). The blue line defines the characteristic pH when aerosol is sensitive to changes in 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 multi-year period reported below each of them: white symbols refer to calculations based on the fog water data and the orange circle the aerosol and gas-phase ammonia data.
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. 2020. Characteristic pH for defining when aerosol is sensitive to changes in 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).