Aerosol pH 25-years trend predicted from fog composition in Po Valley, Italy

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EGU 2020

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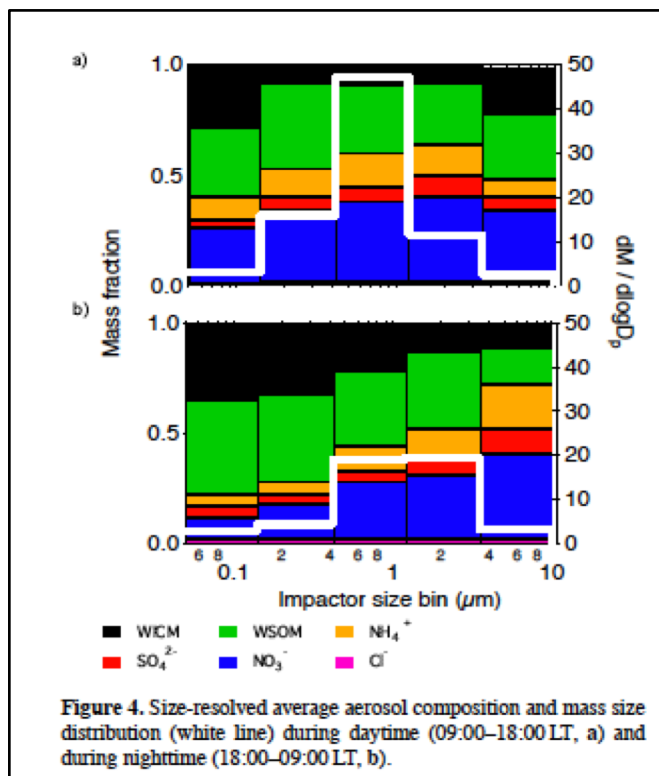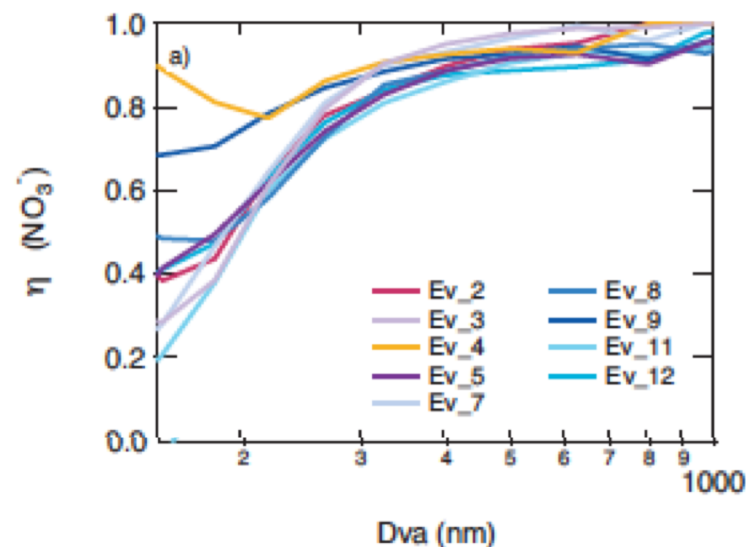
Motivation/approach

Problem: We don't have an aerosol dataset that spans some decades to evaluate the long-term evolution of aerosol pH.

Possible Solution: we can use the fog-water ionic composition as an aerosol proxy *equivalent to a natural – but perhaps a little less efficient "PILS".

Published studies support this, as fog-water collects all aerosol down to about 100nm. Most of the mass that controls pH is scavenged.

Figure 4. Size-resolved average aerosol composition and mass size distribution (white line) during daytime (09:00–18:00 LT, a) and during nighttime (18:00–09:00 LT, b).

Gilardoni et al., ACP, 2014

Figure 7. Mass scavenging efficiency (η) size distribution of nitrate (a) and organics (b) for each fog event; the black line in (b) corresponds to average nitrate scavenging efficiency. D_{va} is vacuum aerodynamic diameter.
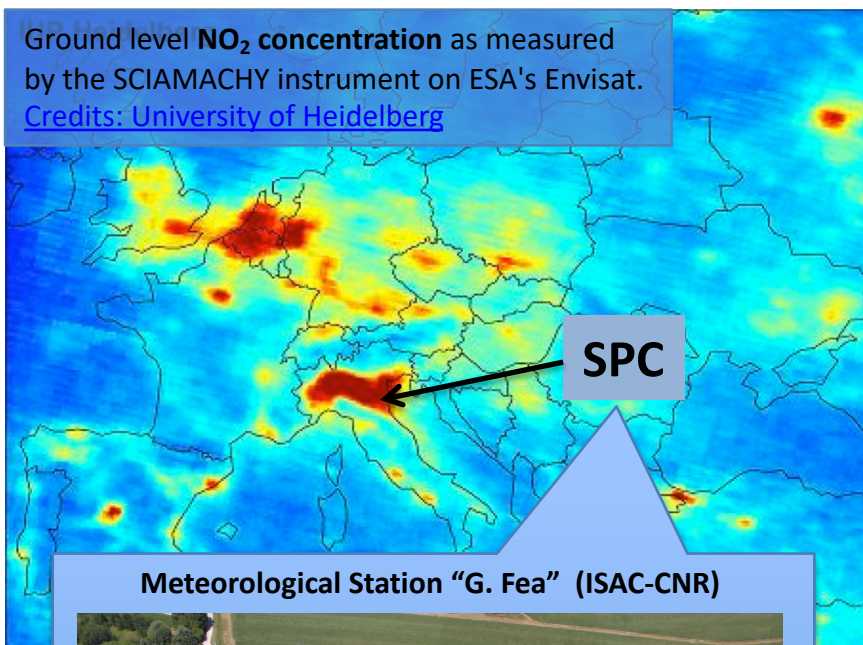
Fog water collection in Po' Valley rural background site San Pietro Capofiume (SPC) since '80

San Pietro Capofiume (SPC) is located about 30 km northeast from the city of Bologna in the Po Valley, the largest industrial, trading and agricultural area in Italy with a high population density. The station itself is in a sparsely inhabited area open to Adriatic Sea to the east side, but enclosed by densely populated areas, on its southern, western and northern sides.

Ground level **NO₂ concentration** as measured by the SCIAMACHY instrument on ESA's Envisat.
Credits: University of Heidelberg

SPC

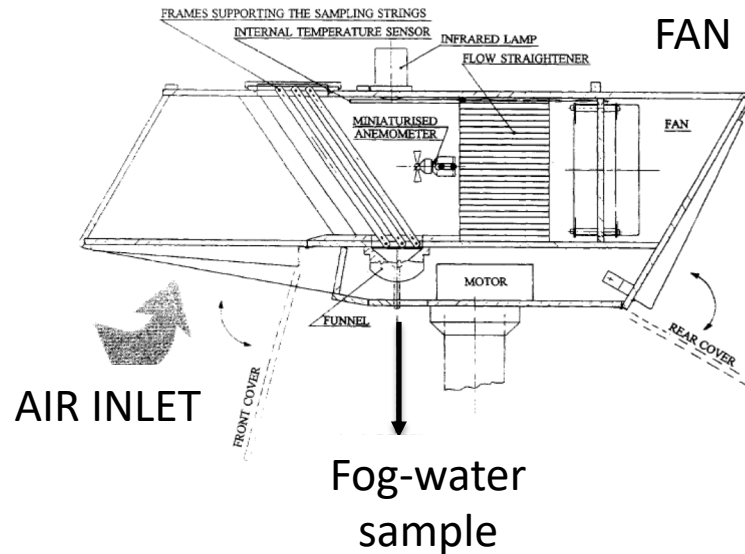**Meteorological Station "G. Fea" (ISAC-CNR)**

Dataset of fog-water composition starting in the early 80s and spanning sistematically from 1993 to 2018

Fog water collection and chemical analyses

Fog-water sampled using an **automated string collector** extensively described in Fuzzi et al. (1997)

A **Particulate Volume Monitor PVM-100**, used to determine **liquid water content of the air** (LWC_{air}) and to activate the string collector.

FRAMES SUPPORTING THE SAMPLING STRINGS
INTERNAL TEMPERATURE SENSOR INFRARED LAMP
FLOW STRAIGHTENER

FAN

MINIATURISED ANEMOMETER

FAN

MOTOR

FUNNEL

REAR COVER

FRONT COVER

AIR INLET

Fog-water sample

Liquid samples are analysed for **inorganic ions (NH4, SO4, NO3, Cl, Na, Ca, K, Mg)** and low molecular weight **organic acids** (acetate, formate, methanesulfonate and oxalate) by ion chromatography (Matta et al., 2003).

Particle concentrations of species in the pre-fog atmosphere (**AerFOG conc.**) are calculated multiplying the concentration in fog-water by the liquid water content of the air (LWC_{air})

AerFOG conc. ($\mu g/m^3$) = Fog-water conc. ($\mu g/mL$) * LWC_{air} (mL/m^3)

Thermodynamic analysis of fog-water composition to obtain prefog aerosol pH

ISORROPIA-II calculates:

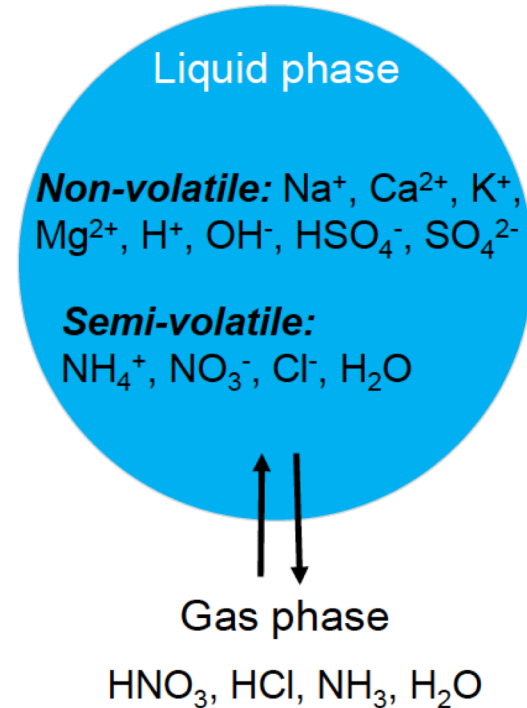the composition and phase state of an NH_4^+-SO_4^{2-}-NO_3^--Cl^--Na^+-Ca^{2+}-K^+-Mg^{2+}-water inorganic aerosol in equilibrium with gases

Assumptions:

- "metastable" aerosol & no phase separation (a single aqueous phase)

- $PM_{2.5}$ in equilibrium with gas

Forward mode:

calculates equilibrium partitioning given total concentration of species (gas + particle)

Liquid phase

Non-volatile: Na^+, Ca^{2+}, K^+, Mg^{2+}, H^+, OH^-, HSO_4^-, SO_4^{2-}

Semi-volatile: NH_4^+, NO_3^-, Cl^-, H_2O

Gas phase

HNO_3, HCl, NH_3, H_2O

http://nenes.eas.gatech.edu/ISORROPIA
(Fountoukis and Nenes, 2007)

Input: Total nitrate (HNO_3+NO_3^-) → Output: HNO_3, NO_3^-

Input: Total ammonium (NH_3+NH_4^+) → Output: NH_3, NH_4^+

$$pH = -\log_{10} \gamma_{H^+} H_{aq}^+ = -\log_{10} \frac{1000\gamma_{H^+}H_{air}^+}{W_i + W_o} \cong -\log_{10} \frac{1000\gamma_{H^+}H_{air}^+}{W_i}$$
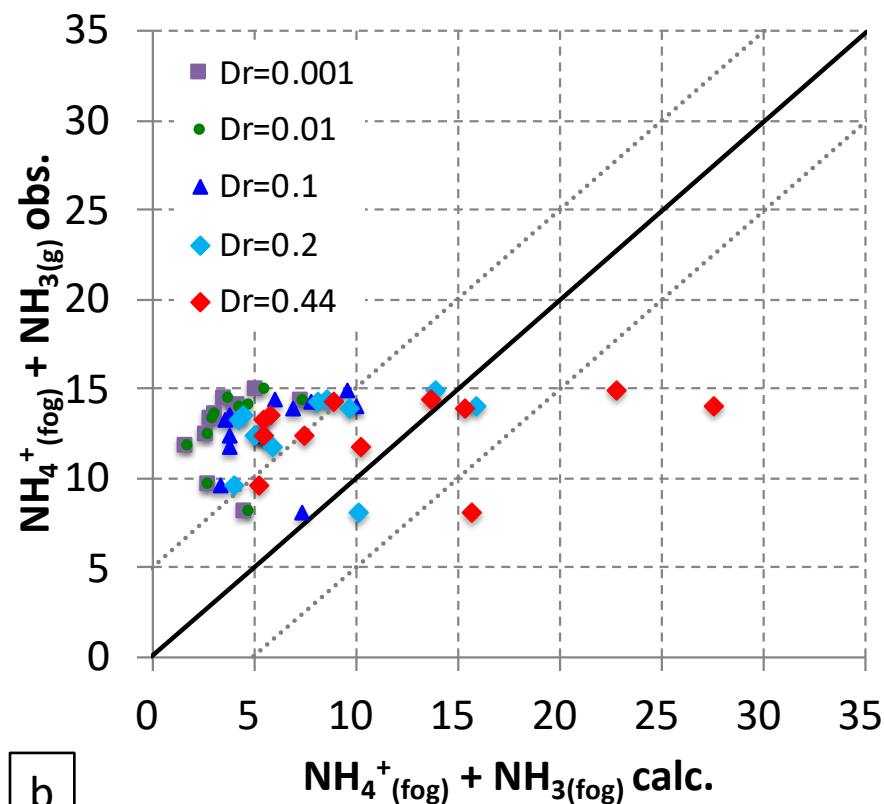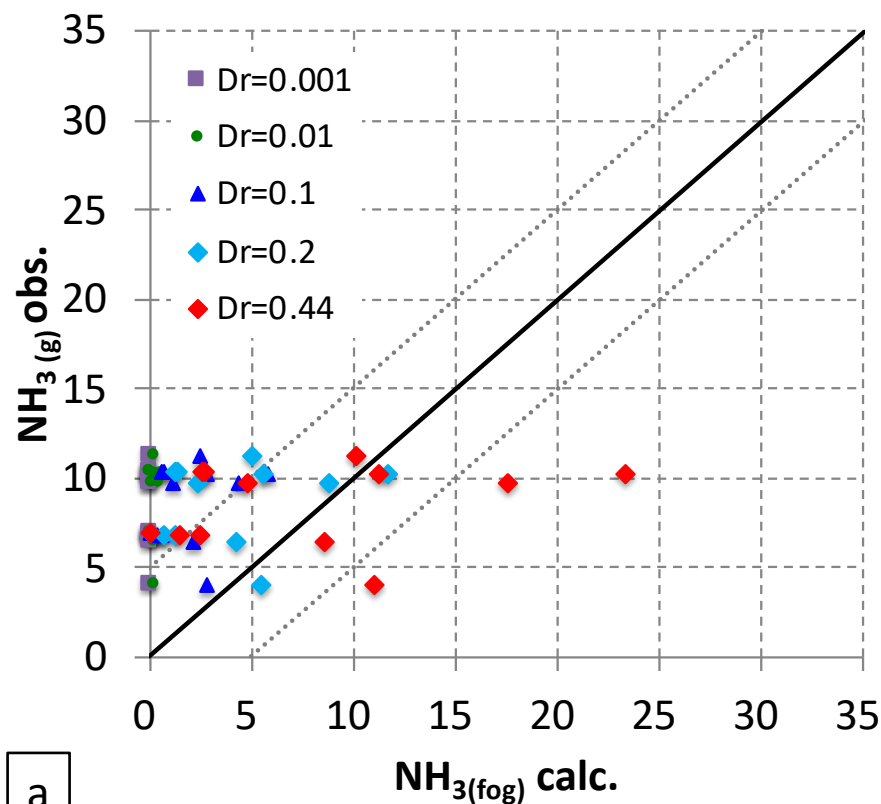
Estimating gaseous ammonia in fogs for use in the thermodynamic analysis

If the atmospheric concentration of gaseous ammonia in fog ($NH_{3,fog}$) is known, it can be included in the thermodynamic analysis.

We determine $NH_{3,fog}$, using the bulk fog-water pH, the Henry's law Coefficient and the measured $LWC_{air,}$ and first assuming that NH_3 is in equilibrium with fog-water NH_4^+.

(1) $$\varepsilon_{NH4} = \frac{H^*_{NH3} RT \, LWC_{\text{fog}}}{1 + H^*_{NH3} RT \, LWC_{fog}}$$

Parameters:
H_{NH3} = Henry's law coefficient (62 M atm^{-1} @298K)
$pKa_{(NH4+)}$= 9.25
[H+] at pKa = 5.6E-10
pH = measured by pH-meter into the liquid fog samples
K_{a1}= 1.7×10^{-5} M

(2) $$H^*_{NH3} = H_{NH3} \frac{K_{a_1}}{K_w} [H^+]$$

(3) $$NH^*_{3(fog)} = \frac{NH^+_{4(fog)}}{H_{NH3} \dfrac{K_{a_1}}{K_w} RT [H^+] LWC_{\text{air}}}$$

Estimating gaseous ammonia in fogs for use in the thermodynamic analysis

If the atmospheric concentration of gaseous ammonia in fog ($NH_{3,fog}$) is known, it can be included in the thermodynamic analysis.

We then correct to account for any apparent departure from this equilibrium (Pandis and Seinfeld, 1991) testing empirically different Deviation ratios (Dr) against $NH_{3(g)}$ measured (Ricci et al., 1998)

a

b

Model Evaluation

In this study to evaluate the predictions of the model we use:

- **188 daily PM2.5 samples between 01Aug2017 & 30Sept2018**
- **Parallel ammonia ($NH_{3(g)}$) measurements**
- **12 FOG water samples collected intermittently in parallel**

Gas-particle partitioning of $NH_{3(g)}$/NH4

2 runs of the model:
- PM2.5 composition+$NH_{3(g)}$
- Fog composition+$NH_{3(fog)}$

ISORROPIA is predicting very well the
partitioning when all the input are provided

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pH predictions PM2.5 vs Fog

pH predicted using:

- **PM2.5 data**:
    - only PM2.5 composition (without gaseous $NH_{3(g)}$) = **AerPM2.5 pH**
    - PM2.5 composition+$NH_{3(g)}$ = **AerPM2.5+$NH_{3(g)}$ pH**

- **Fog data**:
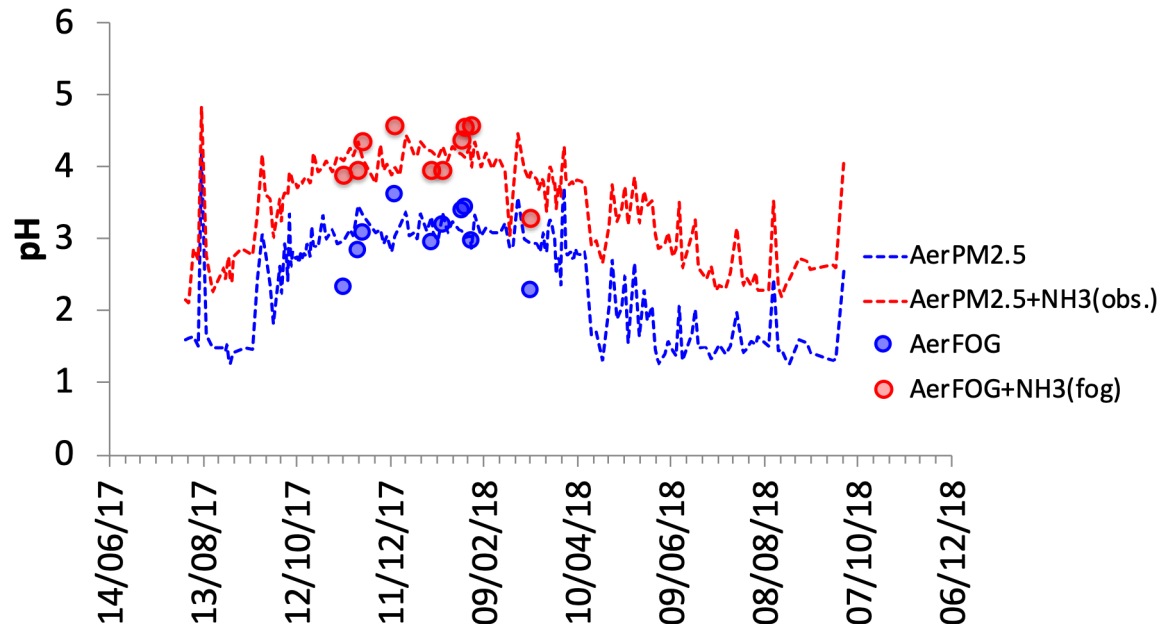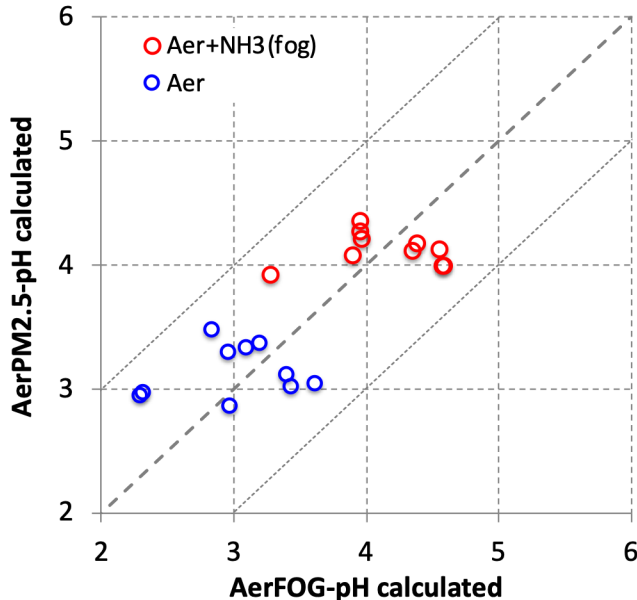   - only fog composition (without gaseous NH_3) = AerFOG pH
    - fog composition+$NH_{3(fog)}$ = **AerFOG+$NH_{3(fog)}$ pH**

Aer**PM2.5+$NH_{3(g)}$ pH ≈ AerFOG+$NH_{3(fog)}$ pH**

➡️ we can use fog composition to estimate pH of aerosol in the pre-fog event atmosphere
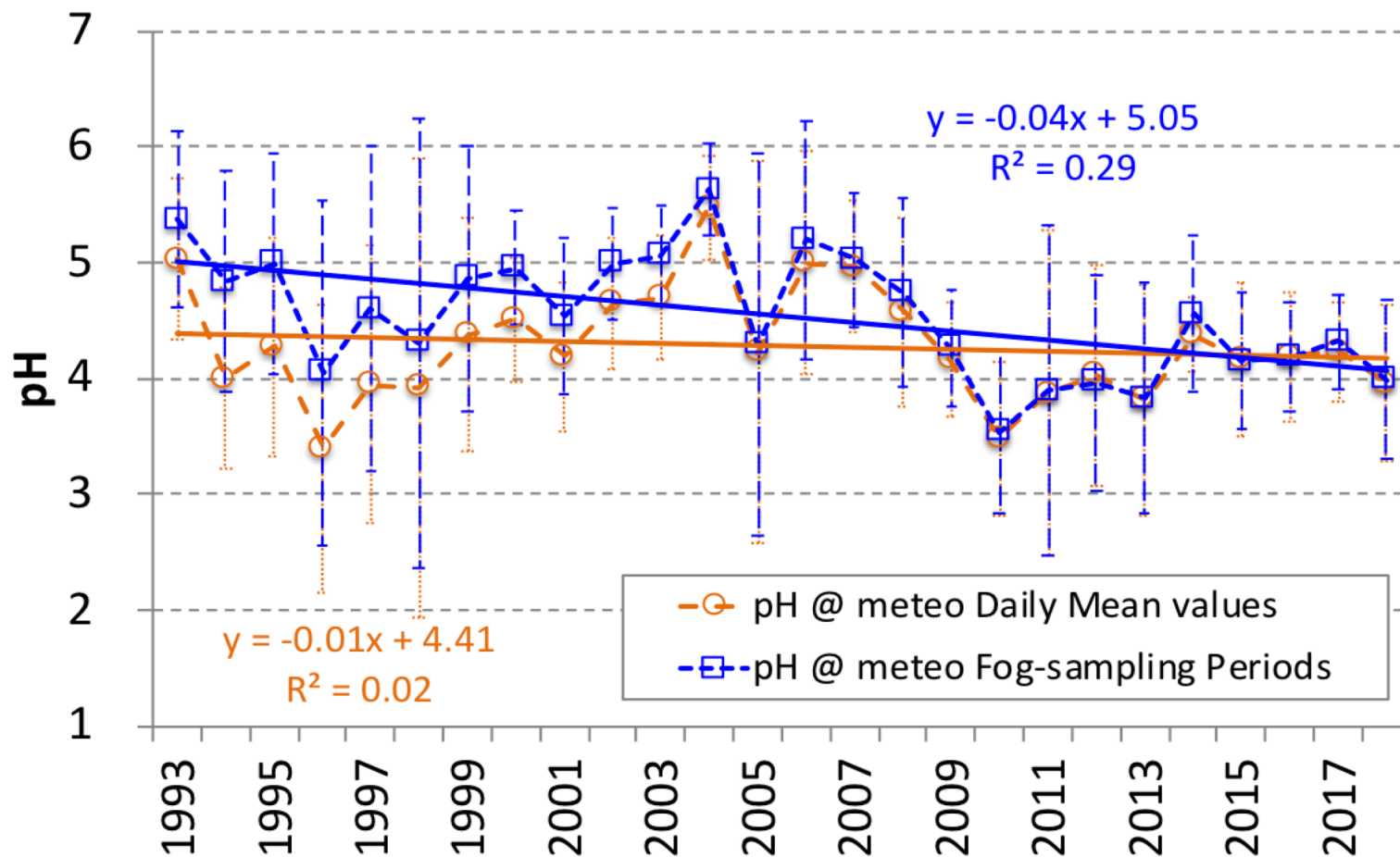

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Aerosol pH trend in the last 25years

560 FOG water samples collected between November and March, from 1993 to 2018 (seasonal median number of samples of 25)

These different trends, although counterintuitive at first glance are consistent with the thermodynamics of the two systems.
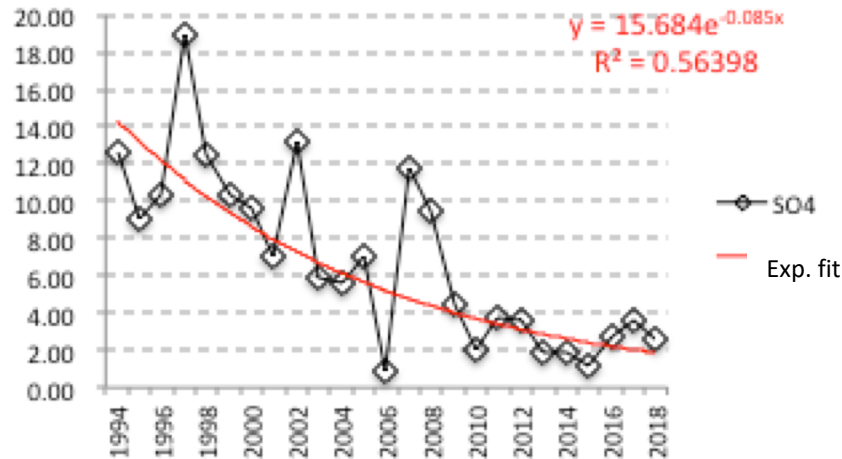
Paglione et al., 2020 in review

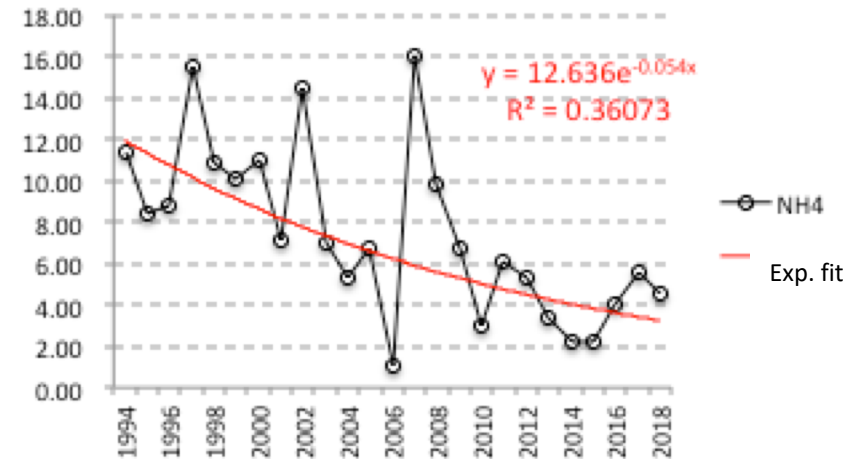# RH and T variability effect on pH predictions

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 1.1-1.5 units over the last 25 years.

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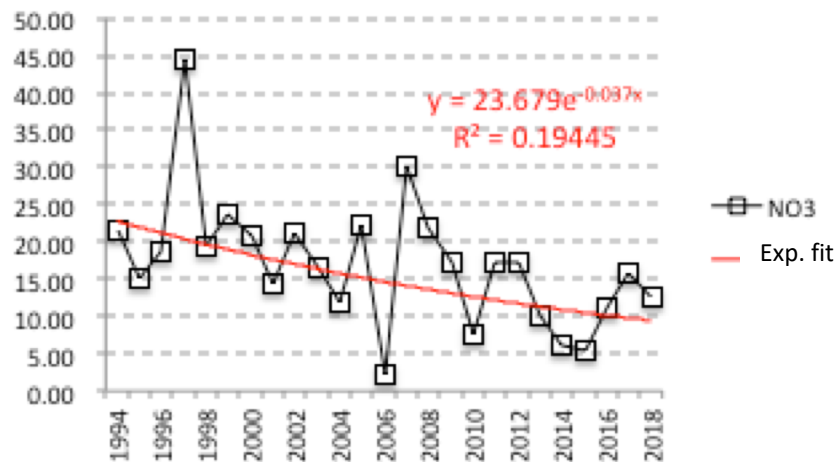
Drivers of the fog and aerosol pH trend: pollutants control and meteo parameters
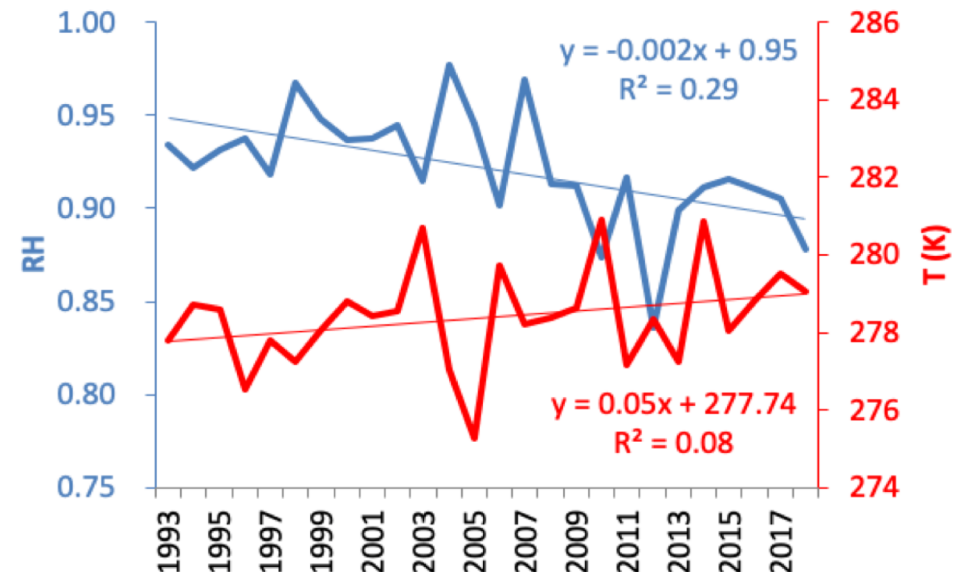
Drivers of the fog and aerosol pH trend: pollutants control and meteo parameters

Multiple linear regression analysis on the simulated aerosol pH (Rosenfeld et al., Science, 2019).
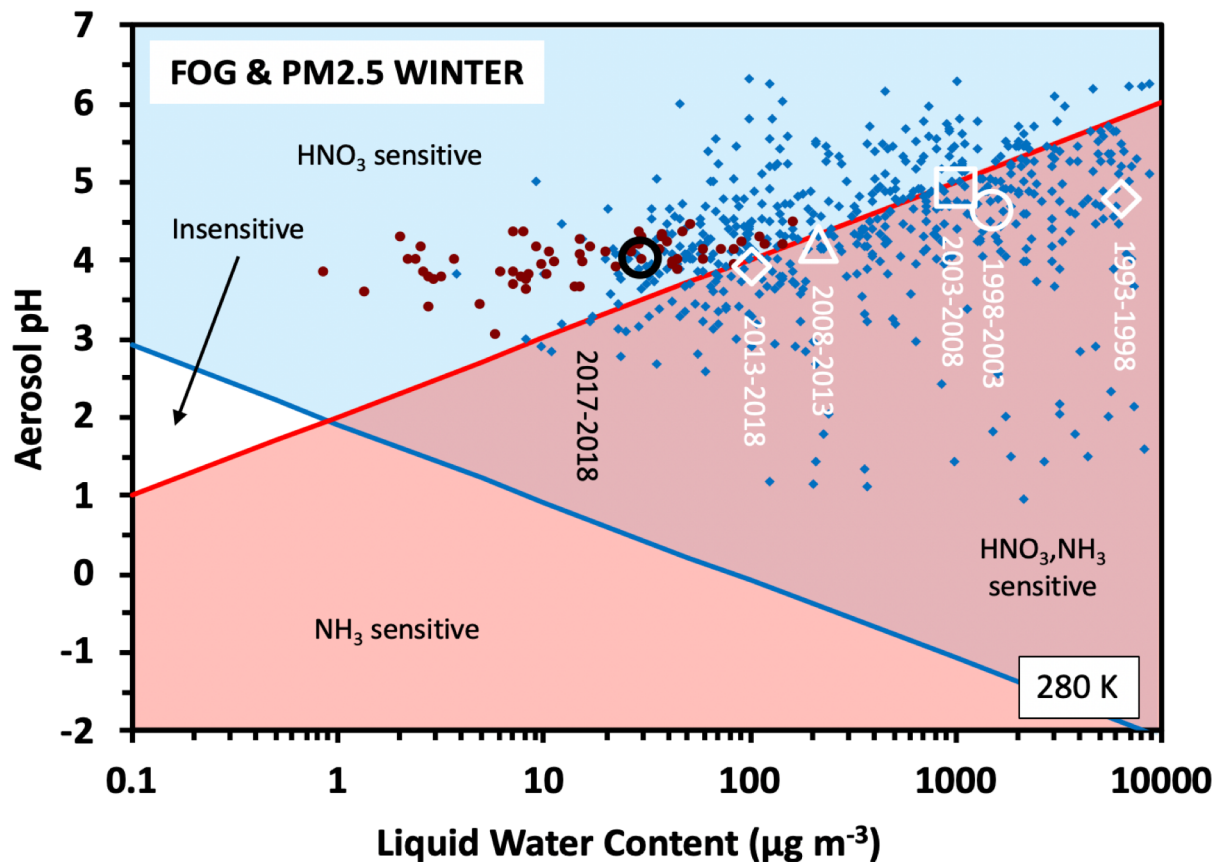
A first regression is applied to the aerosol pH with all the independent variables (ions composition and meteorological parameters) used by ISORROPIA-II in order to calculate the total R^2. The regression is then repeated, sequentially omitting a variable at a time to retrieve the contribution of each individual variable to the total R^2.

		AerFOG pH	
Total R^2		**0.62**	
		Contr.to R^2	**Relative contr.**
Main ions	SO_4^{2-}	0.00	1%
	NH_4^+	0.21	34%
	NO_3^-	0.01	1%
	Cl^-	0.05	8%
NVC	Na^+	0.00	0%
	Ca^{2+}	0.02	3%
	K^+	0.01	1%
	Mg^{2+}	0.05	8%
Meteo	RH	0.01	2%
	T	0.26	41%

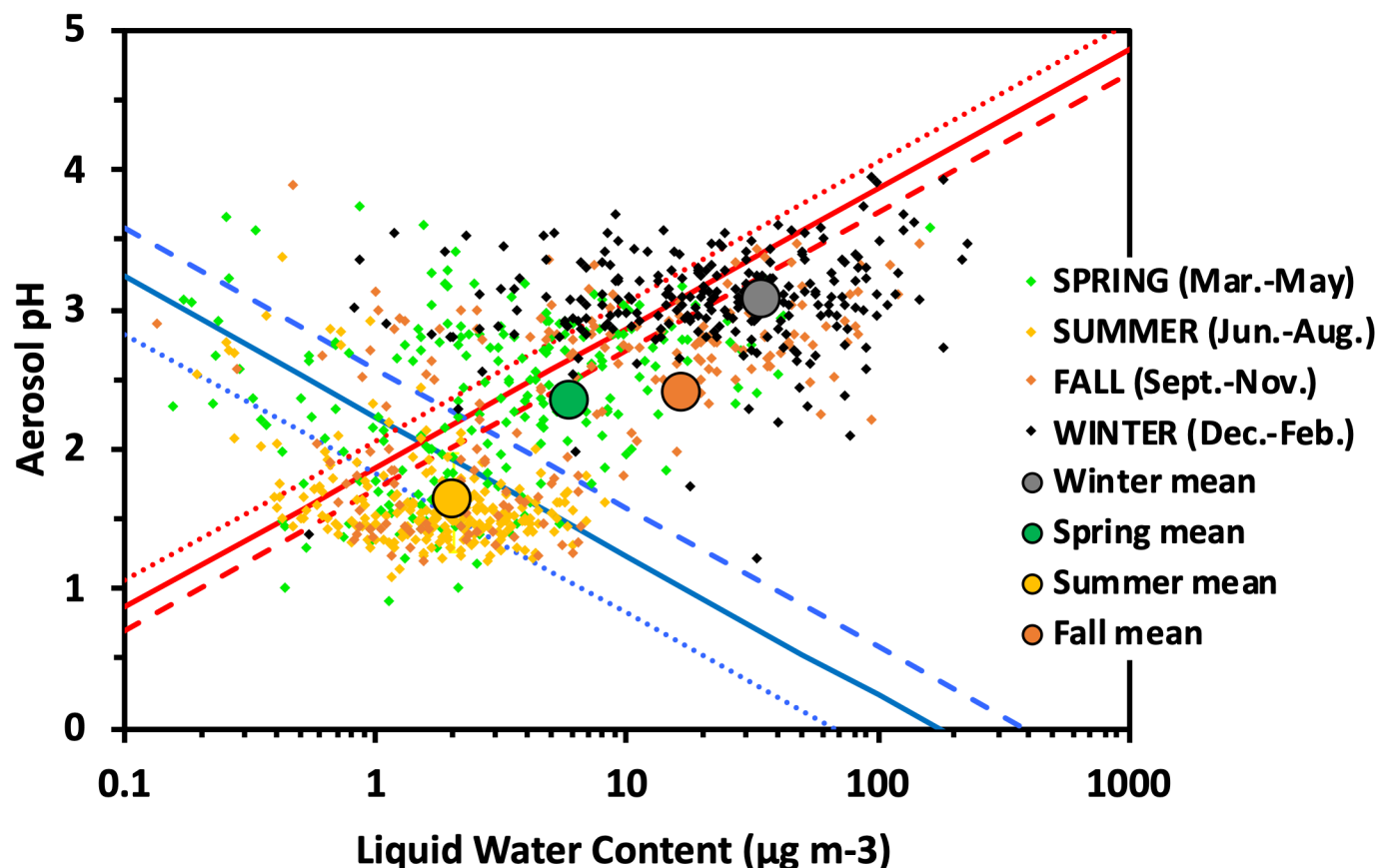# Sensitivity range to ammonia and nitrate availability of Po valley aerosol during winter

The winter-time aerosol has been gradually moving from HNO_3/NH_3-sensitive regimes toward more NH_3 sensitive regime. The aerosol liquid water content in particular has decreased significantly due to changes in PM concentrations and also to decreasing RH.

If the decreasing trend of aerosol pH continues in the future and the pH drops to the sensitivity threshold level, aerosol nitrate will remain almost exclusively in the gas phase as HNO_3, regardless of the amount present, with fundamental consequences on the air quality of the region.

Seasonality of the sensitivity range

The same shift already is taking place in warmer seasons. The PM$_{2.5}$ moves from the HNO$_3$/NH$_3$-sensitive regimes during winter to the NH$_3$ sensitive regime during summer

This seasonality of the PM sensitivity in Po Valley is important about effective pollution control policies, which could be seasonal as well.

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Summary

- For the first time it is suggested the possibility of calculating pre-fog aerosol pH using fog compositional data in a thermodynamically consistent way. This approach can be useful to evaluate long-term trend of particles acidity also in other region of the world for which fog data are available (e.g., Central Valley in CA; etc.)

- Our study shows a decreasing trend in aerosol pH during winter-time in Po Valley in contrast with the increasing trend of bulk fog-water pH. We show for the first time that this increasing pH of cloud/fog may not be indicative of the trend in aerosol acidity.

- The aerosol pH reduction trend is thermodynamically robust and it is driven by the contemporary decrease of the main pollutants atmospheric concentration (due to the environmental policies) and by the changing meteorological parameters (T and RH), possibly linked with climate change.

- If the decreasing trend of aerosol pH continues in the future, it is possible to speculate a shift in the sensitivity range of the aerosol to ammonia and nitrate availability, with fundamental implications on the air quality of the region. If and when this change will happen depends on the rate of future reduction in emissions of NH_3 and NO_x (precursors of ammonia and nitrate) and on the changes of T and RH.