

The chemistry of sulfur and nitrogen species in a fog system

A multiphase approach

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ABSTRACT

Concentration and phase distribution of sulfur and nitrogen species during a particular fog episode in the Po Valley are experimentally described in this paper. Chemical measurements were carried out simultaneously at different heights within the fog layer, up to 50 m. Microphysical and meteorological parameters necessary for the description of the fog multiphase system were also concurrently measured as a function of height. The fog cycle (formation, evolution, dissipation) is described in terms of the total acidity of a unit volume of air containing gas species, interstitial aerosol particles and fog droplets. The fog system was not closed and input of acidic and basic components was observed during fog evolution. The driving force which determines the acidity of the fog multiphase atmospheric system was found to be the presence of NH_3 and its partitioning among the different phases. A strong decrease of fog water pH (from 5.6 down to 2.8) was observed during fog evolution and was attributed to a HNO_3 input to the system. These acidic and basic inputs are described in terms of a titration/back-titration process of the fog system. The SO_2 oxidation process in fog water was found to be of minor importance in determining the SO_4^{2-} concentration within the fog system, due to both low SO_2 concentration and limited oxidant availability during the experiment.

1. Introduction

The fog is a multiphase atmospheric system in which gaseous species, liquid solutions (droplets, wet aerosol) and dry particulate matter coexist. The fog cycle (formation, evolution, dissipation) affects in particular the atmospheric trace com-

pounds which interact with liquid water and redistribute among the different phases as a function of various chemical and microphysical parameters (temperature, fog liquid water content, pH of fog droplets, chemical reactions, etc.).

In this paper we describe experimentally the changes in phase distribution and the chemical reactions of soluble sulfur (SO_2 , S(IV) , SO_4^{2-}) and nitrogen species (NH_3 , NH_4^+ , HNO_2 , HNO_3 , NO_2^- , NO_3^-) within the different reservoirs in the atmosphere (gas phase, fog droplets and interstitial aerosol) during a fog cycle in the Po Valley.

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The nitrogen species NO and NO₂ are not included in our study, since they are not particularly affected by the fog cycle; in fact, given the very low solubility (Schwartz and White, 1981), these compounds are almost 100% partitioned in the gas phase.

In previous papers (Fuzzi, 1986; Fuzzi et al., 1988), we suggested that fog in the Po Valley, which occurs mainly under conditions of high atmospheric stability and very low wind speed, can be viewed as a closed system in which a mass-balance approach could be applied to study the physical and chemical processes occurring within the system itself. However, it was realized that even in these meteorological conditions, the fog system cannot be considered entirely closed, since processes like emission of chemical components within the system, entrainment or advection of air masses of different chemical composition and fog droplet deposition are capable of substantially altering the total concentration of chemical species during a fog episode. Evidence of the above processes in fog is reported by Wobrock et al. (1992), from a meteorological point of view.

Therefore, to obtain a dynamic characterization of the Po Valley fog system, we performed during the present study concurrent measurements of chemical, microphysical and meteorological parameters at different heights (see Fuzzi et al., 1992). The goal of this detailed description is to focus on the principal physical and chemical processes and the most important parameters which control the chemical composition of the fog system and the exchange of material among the different atmospheric reservoirs. The data presented here were collected during the Po Valley Fog Experiment 1989, as part of the EUROTRAC subproject GCE (Ground-based Cloud Experiment).

2. Experimental details

The complete description of the Po Valley Fog Experiment 1989, the set of measurements and the analytical protocols are extensively reported elsewhere (Fuzzi et al., 1992b); here, it is sufficient to summarize the main measurements that will be used in our discussion.

2.1. Gas phase measurements

The wet annular denuder technique (Keuken et al., 1988) was used to sample NH₃ and HNO₃

at three levels: ground, 25 m, 50 m. The time resolution of the measurements was set to one hour in order to match the fog water sampling time (see below). During fog periods, the denuder was equipped with a small cyclone to avoid interference by the droplets. The absorbing solution from the denuder was analyzed by ion chromatography.

SO₂ concentration was also measured at these three levels, using the commercial Monitor Labs 8850 instrument, which, however, was often unable to detect the very low levels of SO₂ present in the air, especially during fog periods. A continuous scrubbing chemiluminescence apparatus with a much lower detection limit (see Fuzzi et al., 1992b for a description of this prototype instrument) was also available to measure SO₂ concentration continuously, but only at the ground level. Only data from this second instrument will therefore be used in our discussion.

Organic acids (formic, acetic and pyruvic) were collected at ground level by an automated version of the mist chamber proposed by Cofer et al. (1985) and analyzed by ion chromatography immediately after sampling in order to avoid microbial decomposition.

2.2. Aerosol sampling

Aerosol samples were collected on aluminum foils by two eight-stage Berner low pressure cascade impactors (Berner et al., 1979), placed at the ground and at 50-m height. The impactors were run round the clock throughout the entire experiment in 3-h time steps. This was the maximum time resolution reasonably possible, given the sampling flow rate of 30 l min⁻¹. After being weighed, the foils were coupled and extracted with deionized water for the subsequent chemical analysis (Fuzzi et al., 1992b). In this way, we obtained from the original eight stages, chemical data in four size ranges (0.06–0.25; 0.25–1; 1–4; 4–16 μm diameter).

2.3. Fog droplet sampling

Fog droplets were collected during the experiment by two single-stage impactors of different design (Winkler, 1986; Berner, 1988), placed at four heights (ground, 10 m, 25 m, 50 m). Sampling duration was standardized to one hour. The discussion of sampling collection efficiency and an intercomparison study between these two collec-

tors is reported elsewhere (Schell et al., 1992). Since the study presented here mainly deals with data from fog event 2 (11–14 Nov.), we will use only the results obtained from the Berner collector (only ground level measurements are available from the Winkler collector during this fog episode). The protocol of fog water chemical analysis is reported in Fuzzi et al. (1992b).

2.4. Fog liquid water content (LWC)

A Particulate Volume Monitor PVM-100 (Gerber, 1984; 1987) was used for direct determination of fog LWC at the ground. LWC at the other levels was measured by integrating the size distribution data provided by a Forward Scattering Spectrometer Probe FSSP-100 run on the tower elevator with a hourly ascent/descendent schedule (Fuzzi et al., 1992b). A correction factor was applied to the LWC values obtained by the FSSP to match the results of the PVM, considered as a reference (Arends et al., 1992). Both PVM and FSSP data were sampled on a one-minute time basis, and were then averaged to match the fog sample collection time (one hour). Short time variations of LWC are discussed in Arends et al. (1992).

3. Results

Five fog events were studied during the Po Valley Fog Experiment 1989 at the FISBAT field station of S. Pietro Capofiume (Fuzzi et al., 1992b). However, to describe the phase partitioning and chemistry of S and N species we will concentrate, as reported above, on a single event that appears to be of particular interest. In Fig. 1, the temporal trends of both LWC and fog water pH during fog event 2 are reported at ground level, 25 m and 50 m. Some interesting features appear from Fig. 1: (a) fog event 2 was characterized by an exceptionally long duration (63 hours); (b) during the central hours of the days 12 and 13 November, fog dissipated at the ground while only a decrease in LWC was observed at the other levels; (c) very different behaviours of fog water pH were observed on the two consecutive days 12 and 13 November. A sharp pH decrease was observed in the period 1100–2300 on 12 November. The pH decreased before the partial dissipation occurred at the ground and remained close to 3 for several hours

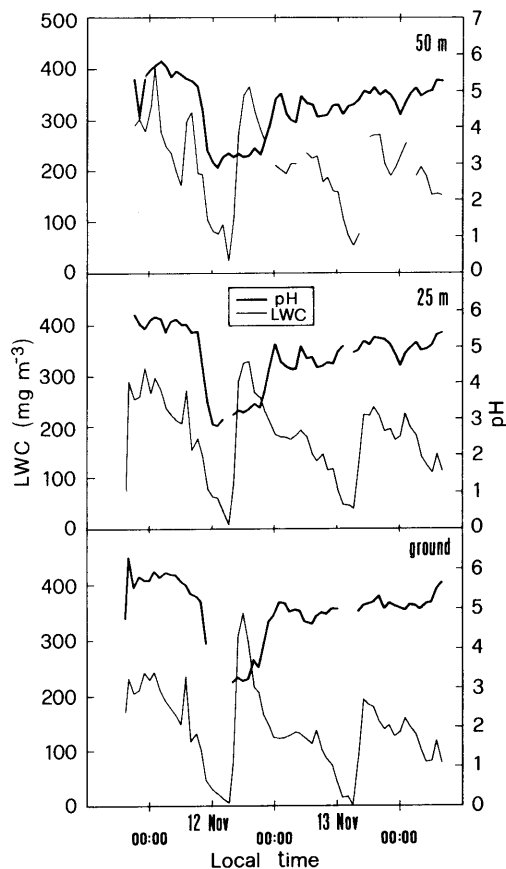


Fig. 1. Temporal trend of fog liquid water content (LWC) and pH during fog event 2 at 3 different levels. The missing pH values at the ground level correspond to the partial dissipation periods (no samples collected). pH data derive from hourly fog samples and LWC results are averaged on the same time basis.

after fog re-intensification. On 13 November on the contrary, no particular pH variations were observed: the fog water pH remained almost constant around 5. The above features are common to all three levels.

In addition, considering the total concentration of the major S and N species in the different phases (Fig. 2), it can be seen that the fog system is not closed, as was hypothesized above. In fact, if the system were closed, the total concentration of the different species in the gas phase, fog droplets and interstitial aerosol would remain constant or decrease due to deposition of material to the ground.

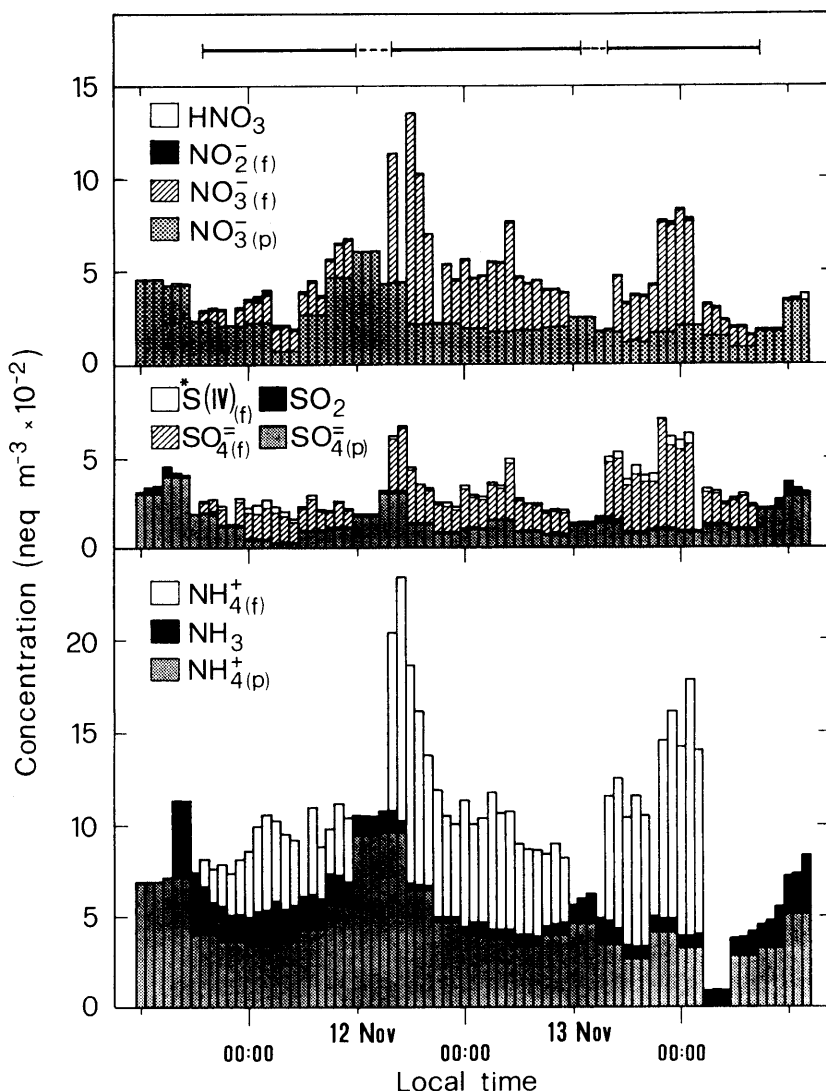


Fig. 2. Total concentration at ground level of the S and N species in the different reservoirs during the fog episode considered in this study. The subscripts (p) and (f) indicate interstitial aerosol particles and fog water, respectively. NH_3 , HNO_3 and SO_2 are the corresponding gaseous species. Gas and fog water concentrations are hourly results, the aerosol particles were collected on a 3-h time basis and the same chemical result is reported 3 times to match the other measurements. The upper bars indicate the duration of fog. The dashed lines between the bars indicate the partial dissipations which took place only at ground level on 12 and 13 November. *Liquid phase S(IV) was not measured and is approximated by HMSA concentration.

3.1. Meteorology

Fog formation started in the afternoon of 11 November. Supersaturation was achieved at ca. 1900 at the ground; fog appearance at the upper levels occurred one hour later, when the tem-

perature at 50 m suddenly dropped 7°C in 10 min, and surface wind speed increased markedly. These observations indicate advection of an already existing foggy air parcel. During the central hours of the day a partial fog dissipation was observed at the ground, both on 12 and 13 November, while at

higher levels fog persisted. These partial dissipations were due to the heating of the surface by solar radiation, which resulted in an upgoing heat flux and warming of the air. The fog re-intensification occurred on both days around 1700 at all levels, and was combined with an increase in horizontal wind speed. The height of the fog layer was nearly constant at 150–180 m on 12 November, while on the next day the upper fog boundary was less stable, sometimes reaching 280 m. The reason for fog dissipation on 14 November around 0900 is not clear; however, it seems likely that advection of drier and warmer air took place, causing the droplets to evaporate. A more exhaustive treatment of the meteorological situation during the experiment is reported by Wobrock et al. (1992).

3.2. Interstitial aerosol

Atmospheric aerosol consists of solid and/or liquid particles depending on ambient relative humidity (R.H.) and on particle chemical composition. A fraction of the atmospheric aerosol serve as condensation nuclei, while those particles for which critical saturation has not been reached remain in the interstitial air. Pandis et al. (1990) pointed out that a distinction in terms of size between interstitial aerosol and aqueous droplets in fog is always arbitrary, since the same physical and chemical processes take place in both aerosol and droplets.

However, in our experiment a cut through the particle size spectrum is unavoidable. In fact, in the presence of fog, a considerable fraction of droplets is collected in the upper stages of the impactors, and this would determine an error in mass balance calculations for the different chemical species. In our calculations, we decided not to use the aerosol size fractions from impactor stages 7 and 8 (4 to 16 μm diameter), in order to avoid overlapping between the lower size cut of the fog collector (ca. 7 μm diameter) and the upper size cut of the aerosol impactor. We are aware that this cut through the size spectrum of droplets and aerosol is arbitrary to some extent and is only instrumental to the description of our system. Although a minor fraction of activated fog droplets is taken into account as interstitial aerosol, we do not expect any major error in terms of the mass of the different chemical species.

It should also be pointed out that the ambient

aerosols are collected by the multistage impactor as a function of their wet size, i.e., the actual size at ambient R.H. However, the mass and chemical composition of the deposited particles are determined once the liquid water associated with the particles has evaporated at room temperature. This fact may induce changes in the chemical composition of the particles. These changes depend on the initial chemical composition and liquid water fraction of each individual particle, and on the atmosphere in which the particles evaporate. It is therefore impossible to study the aerosol-gas-droplet mass distribution of the different chemical species by a rigorous thermodynamical procedure (Bassett and Seinfeld, 1983; Pilinis and Seinfeld, 1987).

On the other hand, through nucleation scavenging aerosol particles largely determine the composition of the droplets in the early stage of fog formation (Noone et al., 1992; Hallberg et al., 1992), even if a considerable fraction of the aerosol is not incorporated by the droplets (Noone et al., 1992). While aware of the above limitations of our aerosol results, we will include them in our calculations, mainly in the form of bulk data.

3.3. Gas phase

The temporal trends of R.H. and of gaseous NH_3 , HNO_3 and SO_2 (chemiluminescence technique) concentrations at the ground are presented in Fig. 3, for the entire period of the experiment. The trend of gaseous species concentration at the other levels is reported elsewhere (Fuzzi et al., 1992b); SO_2 measurements with the chemiluminescence technique were performed only at the ground, as reported above.

Gaseous HNO_3 concentrations range between 9 (DL) and 41 nmol m^{-3} throughout the period. This is not surprising, given the high solubility of HNO_3 in water at all pHs (Schwartz and White, 1981). From Fig. 3, we see that in our case gas phase HNO_3 concentration is above DL only when R.H. is lower than 80%. This indicates that HNO_3 is incorporated into the wet aerosol particles well before fog formation.

NH_3 and SO_2 partitioning between gas and liquid phase, on the contrary, is strongly pH dependent (Hales and Sutter, 1973; Hales and Drewes, 1979).

Gaseous NH_3 is present in a concentration range of 20–1200 nmol m^{-3} , and, although the

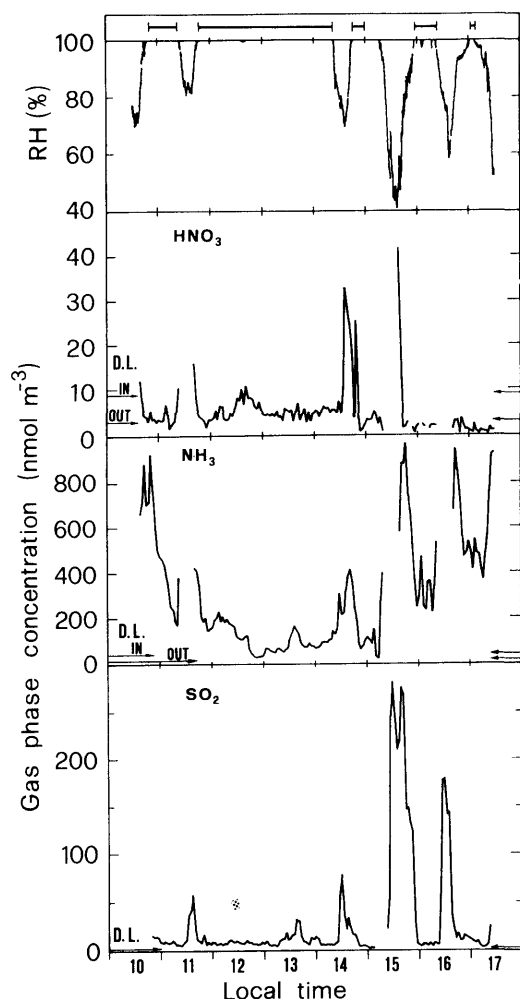


Fig. 3. Temporal trends of R.H. and of the ground level concentrations of HNO_3 , NH_3 and SO_2 , for the whole duration of the experiment. The detection limits (DL) for the different species are reported; in the case of HNO_3 and NH_3 (denuder measurements) two distinct DLs were calculated during fog and out-of-fog periods. The five fog events studied during the experiment are indicated by the upper horizontal bars; the two partial dissipations occurring at the ground during fog event 2 are not shown in this figure. The figures reported in abscissa indicate the days during the month of November, 1989 (local time).

effect of dissolution in the liquid phase is evident when fog is present (Fig. 3), a substantial partial pressure of NH_3 can co-exist in the air with the presence of liquid droplets. If we compare the theoretical and experimental pseudo-Henry's law

constants (K_H^*) (Schwartz, 1984) as a function of pH for the complete set of $\text{NH}_4^+/\text{NH}_3(\text{g})$ data collected during the present experiment (Fig. 4), it can be seen that deviations from equilibrium conditions are particularly large in the pH region below 4.5 (up to 2 orders of magnitude less than predicted values); above pH 4.5 deviations not larger than a factor of 10 are observed, in both positive and negative directions. It should be noted that the same effect was observed, in a different pH range, for the case of organic acid and formaldehyde gas/liquid equilibria (Facchini et al., 1992). It is therefore important to evaluate whether these non-equilibrium conditions are real or derived from experimental artifacts.

Contamination of the denuder absorption solution by fog droplets, especially those with a high NH_4^+ content produces an overestimation of gaseous NH_3 concentration (the size cut of the cyclone used to exclude fog droplets from the denuder inlet is $4\text{ }\mu\text{m}$). In Fig. 4, the effect of this artifact on the experimental K_H^* is shown: the error bars (in the positive direction) are calculated assuming a maximum contamination of fog droplets of 1% and of aerosol mass of 4% ($1\text{--}4\text{ }\mu\text{m}$ diameter range). These assumptions derive from wind tunnel tests prior to the experiment. The effect of contamination produces larger errors in the lower pH region, but this still does not explain the larger deviations observed. In Fig. 4 the line indicated as CV represents the critical value above which K_H^* cannot be determined from experimental measurements due to the gas phase NH_3 detection limit. This limits the possibility of studying the region of pH below 4.5, in which larger deviations are observed, and prevents any definitive conclusion on the reliability of the experimental K_H^* . Other possible explanations of the above non-equilibrium conditions could be related to a discrepancy between the measured bulk fog water pH and the actual pH of the individual fog droplets (Perdue and Beck, 1988). Pandis and Seinfeld (1991) calculated that this effect would produce a bulk fog water solution supersaturated with respect to NH_3 ; the large departures that we observe in the pH range below 4.5 are however in the opposite direction. Winiwarter et al. (1992) argued that the high variability of LWC in fog on a short time basis can account for an undersaturation effect of bulk fog water samples of up to a factor of 20. Nonetheless,

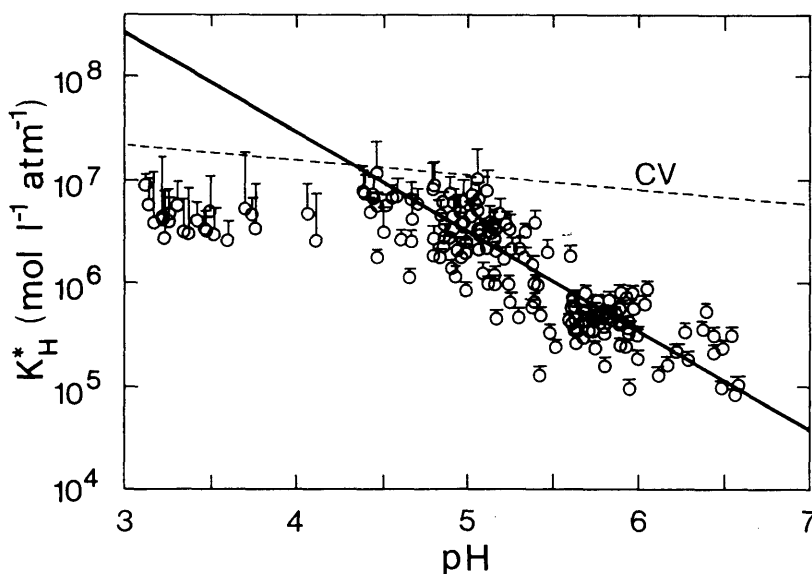


Fig. 4. Theoretical (solid line) and experimental (open circles) pseudo-Henry's law constant for the NH_3 gas/liquid partitioning as a function of pH. The theoretical K_H^* is defined as:

$$K_H^* = K_H \left(1 + \frac{K_b[H^+]}{K_w} \right),$$

where K_H is the Henry's law constant (Dasgupta and Dong, 1986), K_b is the basic dissociation constant of NH_3 in solution, K_w is the dissociation constant of water and $[H^+]$ is the hydrogen ion concentration in solution. The open circles represent the experimental $K_H^* = [\text{NH}_4^+]_{(l)}/[\text{NH}_3]_{(g)}$, calculated from concurrent gas and liquid phase measurements (1-h time basis). The experimental results represent the entire set of data collected during the experiment. The dashed line represents the critical value (CV) above which experimental K_H^* cannot be evaluated (see text). The error bars, calculated as reported in the text, are also shown.

this effect cannot entirely account for the large departures from Henry's law equilibrium observed in our samples. Changes in the composition of the bulk fog water solution due to outgassing of NH_3 (Pandis and Seinfeld, 1991) and temperature changes from the field to the laboratory would also produce deviations with respect to the initial atmospheric conditions, but these effects are difficult to quantify. The presence of an organic film on the surface of fog droplets (Chang and Hill, 1980; Gill et al., 1983) can result in mass transport limitation across the air/droplet interface; the magnitude of this effect increases when the partitioning equilibrium shifts towards the liquid phase (low pH region for NH_3), and a higher mass transfer across the gas/liquid interface is expected. Hydrophobic organic substances have recently been detected in polluted fogs (Capel et al., 1990;

1991). The presence of such species, capable of producing an organic film on the surface of fog droplets, is likely to occur also in the high pollution conditions of the Po Valley.

Gaseous SO_2 concentration exhibits a diurnal trend with maxima during the central hours of the day, reaching concentrations up to 330 nmol m^{-3} in clear air conditions. SO_2 concentration during fog periods is very low, sometimes close to the DL of the more sensitive chemiluminescence technique.

3.4. Fog water

Three species alone, NH_4^+ , NO_3^- and SO_4^{2-} , account for ca. 90%, on average, of the total fog water ionic strength, in agreement with previous fog experiments carried out in the Po Valley (Fuzzi, 1988; Fuzzi et al., 1985; 1988; 1990; 1992a).

The concentration temporal trends (in meq l^{-1}) of these species at the different levels during fog event 2 are reported in Fig. 5, along with the measured fog water pH. At the time of the two partial dissipations, evidenced by the missing pH data in the ground level graph (no sample collected), there is a strong increase of the fog water concentration of all species. This increase is due in part to the decrease in LWC (see Fig. 1) but is not entirely accounted for by this parameter. In particular, the ratio $[\text{NO}_3^-]/[\text{SO}_4^{2-}]$ ranges for all levels throughout fog event 2 from 0.5 to 1.5, but increases to 4 in the period corresponding to the

first partial dissipation, where the pH drops to values around 3 (12 November from 1100 to 2300). The increase in the ratio $[\text{NO}_3^-]/[\text{SO}_4^{2-}]$ is due to a much higher NO_3^- concentration. Such a high $[\text{NO}_3^-]/[\text{SO}_4^{2-}]$ ratio is observed only during this brief period in the entire duration of the experiment (Fuzzi et al., 1992b) and the coincidence with the lowest measured fog water pH values suggests the possibility of a connection between the two experimental observations (see below).

The results presented so far provide a description of the chemistry within the different phases which constitute the fog system. However, to account for the dynamical evolution of the system as a whole, a quantitative approach is needed, which also takes into account the mass exchanges among the phases, i.e., a multiphase approach.

4. Atmospheric acidity. A useful tool to describe the distribution of the chemical species among the different phases

4.1. Definitions

The concept of atmospheric acidity was first introduced by Liljestrand (1985) and later employed by Jacob et al. (1986) and Behra et al. (1989). Atmospheric acidity ($[\text{ACY}]$) is defined as the base neutralizing capacity ($[\text{BNC}]$) of a unit volume of an atmospheric system, including gas-interstitial aerosol- and droplet-phases (Stumm and Morgan, 1981), and is calculated as the sum of the concentration of all species (in all phases) containing "excess" protons minus the concentration of all species with proton "deficiency", with respect to a proton reference level. In analogy with $[\text{ACY}]$ and $[\text{BNC}]$, the concepts of atmospheric alkalinity ($[\text{ALK}]$) and of acid neutralizing capacity ($[\text{ANC}]$) can be defined:

$$[\text{ALK}] = -[\text{ACY}] \quad (1)$$

and

$$[\text{ANC}] = -[\text{BCN}]. \quad (2)$$

$[\text{ACY}]$ is therefore a multiphase concept and can be applied to a dynamic system which is not closed as in the case of our fog (see Fig. 2) and where acidic and basic species can be introduced into the system (gas and aerosol input) or be produced

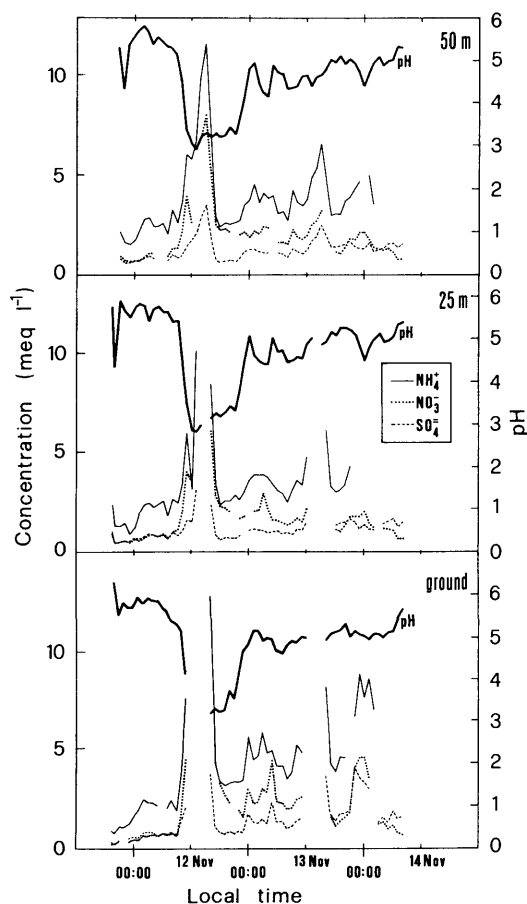


Fig. 5. Temporal trends of major ion concentration in fog water at 3 different heights during fog event 2; fog water pH is also reported. The missing pH values at the ground level indicate the two partial dissipations occurring on 12 and 13 November. The reported data are hourly values.

within the system itself (local sources and chemical reactions). The addition of new components during the evolution of the multiphase system can be described as a function of time in analogy with a titration curve (see Subsection 5.2).

4.2. Reference system

[ACY] is the sum of aerosol acidity [Acy]_a, gas acidity [Acy]_g and fog water acidity [Acy]_f (when fog is present). To calculate [ACY] of a system, it is necessary to define, as reported above, the proper proton reference level for the different phases (Stumm and Morgan, 1981).

gas reference level:



aerosol reference level:

"neutralized" solution containing the species: NH_4^+ , K^+ , Na^+ , Ca^{++} , Mg^{++} , $\text{SO}_4^{=}$, NO_3^- , Cl^- .

fog water reference level:

"neutralized" solution containing the species NH_4^+ , K^+ , Na^+ , Ca^{++} , Mg^{++} , $\text{SO}_4^{=}$, S(IV), NO_2^- , NO_3^- , Cl^- , undissociated HCOOH and CH_3COOH , $\text{CO}_{2(g)}$. In our system [S(IV)] is approximated by [HMSA⁻] (Facchini et al., 1992).

In the following discussion, the concentration of the various species in the different phases will all be reported in units of neq m^{-3} and represented in square brackets, regardless of the phase that the particular component belongs to. The different phases are identified by the subscripts: a (aerosol), g (gas), f (fog), aq (physically dissolved gas species). The use of concentration values in neq m^{-3} implicitly takes into account the charge of the different ions. The definition in terms of neq m^{-3} concentration of gaseous and particulate species is straightforward; to convert the measured fog water concentrations into units of neq m^{-3} , the following expression was applied:

$$[X]_f (\text{neq m}^{-3}) = [X] (\mu\text{eq l}^{-1}) \times \text{LCW} (\text{ml m}^{-3}), \quad (3)$$

where [X] is the measured concentration of X in fog water.

4.3. Fog water acidity ([Acy]_f)

Fog water acidity is defined, with respect to the above reported reference level:

$$\begin{aligned} [\text{Acy}]_f &= [\text{H}^+]_f - [\text{HCOO}^-]_f \\ &\quad - [\text{CH}_3\text{COO}^-]_f - [\text{HCO}_3^-]_f \\ &\quad - [\text{CO}_3^{=}]_f - [\text{NH}_3]_{\text{aq}} - [\text{OH}^-]_f \\ &= [\text{H}^+]_f - [\text{An}^-]_f - [\text{NH}_3]_{\text{aq}}. \end{aligned} \quad (4)$$

The term $[\text{CO}_3^{=}]_f$ is always negligible in the pH range of atmospheric interest and can therefore be omitted. From the concept of electroneutrality also the following relation applies:

$$[\text{Acy}]_f = [A^-]_f - [C^+]_f - [\text{NH}_3]_{\text{aq}} \quad (5)$$

where $[A^-]_f$ is the sum of concentrations of the conservative anions plus HMSA concentration:

$$\begin{aligned} [A^-]_f &= [\text{Cl}^-]_f + [\text{NO}_2^-]_f + [\text{NO}_3^-]_f \\ &\quad + [\text{HMSA}^-]_f + [\text{SO}_4^{=}]_f \end{aligned} \quad (6)$$

and $[C^+]_f$ is the sum of NH_4^+ concentration plus the concentration of conservative cations:

$$\begin{aligned} [C^+]_f &= [\text{NH}_4^+]_f + [\text{K}^+]_f + [\text{Na}^+]_f \\ &\quad + [\text{Ca}^{++}]_f + [\text{Mg}^{++}]_f. \end{aligned} \quad (7)$$

$[\text{NH}_4^+]_f$, however, represents over 90% of the total cation concentration in our fog water, so that $[C^+]_f$ can be approximately by $[\text{NH}_4^+]_f$. Therefore, combining the eqs. (4) and (5):

$$\begin{aligned} [\text{Acy}]_f &= [\text{H}^+]_f - [\text{An}^-]_f - [\text{NH}_3]_{\text{aq}} \\ &= [A^-]_f - [\text{NH}_4^+]_f - [\text{NH}_3]_{\text{aq}} \end{aligned} \quad (8)$$

$[\text{Acy}]_f$ is then calculated from the measured fog water concentrations (right-hand term of eq. (8)).

4.4. Aerosol acidity ([Acy]_a)

Aerosol acidity is defined as:

$$[\text{Acy}]_a = [A^-]_a - [C^+]_a \quad (9)$$

where:

$$[A^-]_a = [\text{Cl}^-]_a + [\text{NO}_3^-]_a + [\text{SO}_4^{=}]_a \quad (10)$$

and

$$[C^+]_a = [NH_4^+]_a + [K^+]_a + [Na^+]_a + [Ca^{++}]_a + [Mg^{++}]_a \quad (11)$$

All parameters in eq. (9) are experimentally determined.

4.5. Gas acidity ($[Acy]_g$)

Gas acidity is defined with respect to the atmospheric partial pressure of CO_2 , as:

$$[Acy]_g = [HNO_3]_g + [SO_2]_g + [HCOOH]_g + [CH_3COOH]_g - [NH_3]_g. \quad (12)$$

The parameters of eq. (12) are experimentally determined (organic acid and SO_2 gaseous concentration only at the ground level).

5. Discussion

From the data collected during the experiment, and using the above reported relations, it is possible to describe in terms of $[ACY]$ the dynamical behaviour of the atmospheric system under investigation, in this particular case the fog event 2.

5.1. Temporal trend of the acidity in the multiphase system

Hourly data are available for gas and fog water measurements, while the aerosol samples were collected on a three-hour time basis. Scaling-up gas- and liquid-phase measurements to the less time-resolved aerosol measurements would considerably limit the possibility of describing the dynamical physico chemical processes taking place within the system. On the other hand, $[Acy]_a$ ranges from +50 to -50 neq m^{-3} (with an average value of 9 neq m^{-3}), which is a minor contribution to the overall $[ACY]$ of the system, as will be shown below. We will therefore neglect the contribution of the interstitial aerosol to the $[ACY]$ of the system, also in light of the considerations reported in Subsection 3.2, i.e., the possibility that the sampling technique could alter the chemical composition of the particles. This limitation implies that it is not possible to describe rigorously in terms of $[ACY]$ the fog formation

period (nucleation scavenging). The fog formation period in the Po Valley, and in particular for the event that we want to analyse, is relatively short: <1 h, and the time resolution of our analysis is 1 h.

Therefore, in pre-fog conditions:

$$[ACY] = [Acy]_g, \quad (13)$$

while in the presence of fog:

$$[ACY] = [Acy]_g + [Acy]_f. \quad (14)$$

Eq. (14), from the combination of eqs. (8) and (12) becomes:

$$[ACY] = [A^-] - [NH_4^+] - [NH_3]_{aq} + [HCOOH]_g + [CH_3COOH]_g + [HNO_3]_g + [SO_2]_g - [NH_3]_g. \quad (15)$$

From thermodynamic considerations, gas phase HNO_3 is not expected to exist in the presence of liquid droplets (Fig. 3), therefore this term can be neglected in eq. (15).

A temporal plot of $[ACY]$ calculated for three different heights from eqs. (12) and (15) is reported in Fig. 6. The reported time period spans from 11 November at 1200, a few hours before fog formation, to 14 November at 1200, after fog dissipation. Missing data indicate that one or more of the parameters needed for the calculations are missing. The high number of missing data at the 50 m level derives mainly from a malfunction of the automated wet denuder during the period.

Before fog formation, the system had a net alkaline character and exhibited a higher $[ALK]$ (negative $[ACY]$) at the ground with respect to 25 and 50 m. This derives from the negative gradient of $NH_{3(g)}$ concentration with height, which was always observed before the establishment of the temperature inversion (Fuzzi et al., 1992b).

Fog formation resulted in a limited $[ACY]$ increase, probably due to the effect of aerosol scavenging, which we cannot follow due to the above reported approximations. Oscillations in $[ACY]$ (negative) took place until 0300–0400 on 12 November. Starting from 0600 an increase in $[ACY]$ was observed at all levels. This steady increase persisted for several hours, through the partial dissipation (ground level only), to ca. 1800 on the same day. The net $[ACY]$ increase of the

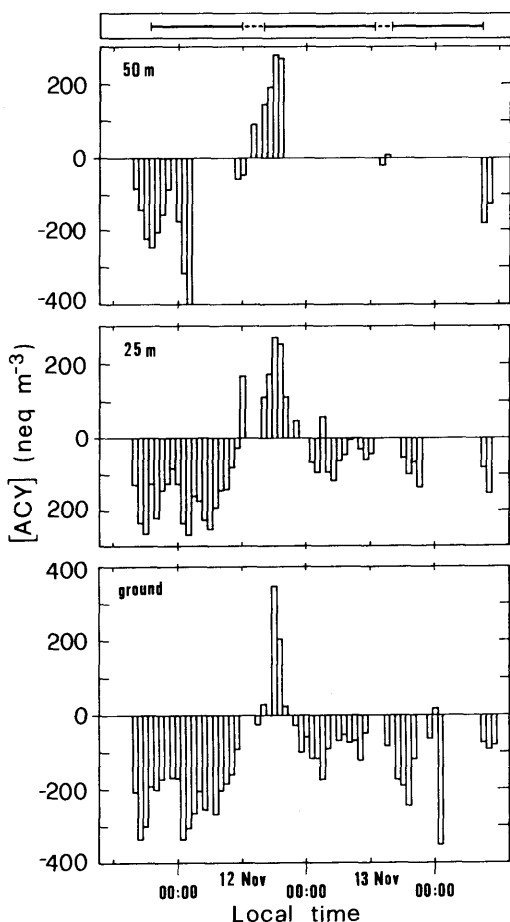


Fig. 6. Temporal trend at three different heights of total atmospheric acidity ($[ACY]$) before, during and after fog event 2. $[ACY]$ is calculated from eqs. (12) (out-of-fog periods) and (15) (in the presence of fog); missing data in this figure indicate that one or more of the parameters in eqs. (12) and (15) are missing. The high number of missing data at the 50-m level are mainly due to a malfunction of the denuder during that period (NH_3 and HNO_3 results). The reported results derive from hourly measurements. Fog duration is indicated by the upper bars; the dashed lines between the bars indicate the partial dissipations which took place only at the ground level during this fog episode.

system over this time interval is quantified in approx. 500 neq m^{-3} (from ca. -200 to ca. 300). The maximum $[ACY]$ level was reached at 1800, after which time a drastical reduction of $[ACY]$ to ca. -100 neq m^{-3} took place in a few hours (approx. till 2300). Following this period, $[ACY]$

oscillated around this last value until the end of the event.

It is useful to compare the contributions of $[Acy]_g$ and $[Acy]_f$ to the $[ACY]$ of the whole system. Fig. 7 reports the temporal trend of both $[ACY]$ (solid line) and $[Acy]_f$ (histogram) over the 63 h of fog duration (from 1900 on 11 November to 0900 on 14 November). The trend of fog water free acidity, derived from measured fog water pH, is also reported in the figure. $[ACY]$ is

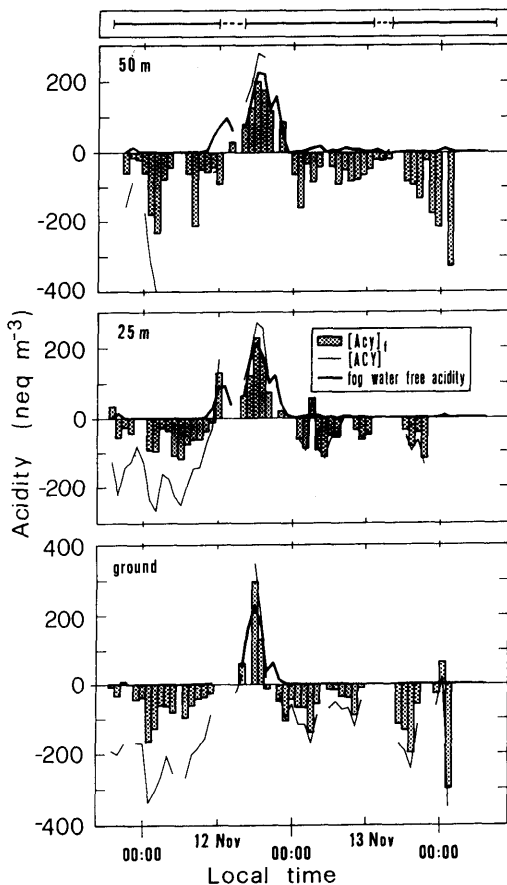


Fig. 7. Temporal trends at three different heights of total atmospheric acidity ($[ACY]$ from eq. (15)), fog-water acidity ($[Acy]_f$ right term of eq. (8)) and fog-water-free acidity (from pH measurements) during fog event 2. The average pH of the proton reference level of the fog system ($[ACY]=0$) is 4.5. The reported results derive from hourly measurements. Fog duration is indicated by the upper bars; the dashed lines between the bars indicate the partial dissipations which took place only at the ground level during this fog episode.

the same as in Fig. 6, while $[Acy]_f$ is calculated from experimental data using the right term of eq. (8).

A considerable fraction of the $[ANC]$ of the system during the first period of fog (until the first partial dissipation) was provided by the gas phase (contribution of $NH_{3(g)}$ in equilibrium with fog water). The increase in $[ACY]$ to values around 300 neq m^{-3} (slightly different at the three different heights) was undoubtedly due to an acid addition. The effect of acid addition to the system caused the depletion of the $[ANC]$ of the system itself, as well as a depletion of the gaseous NH_3 reservoir (see Fig. 3). In the period of positive $[ACY]$, $[Acy]_f$ coincided fairly well with fog water free acidity (pH); this means that the acidity of the system was due to strong acids in solution. The difference between $[Acy]_f$ and $[ACY]$ was due to the organic acid gas concentration, which enhanced the $[BNC]$ of the system with respect to fog water. Organic acid measurements were carried out only at the ground, these values were also used for the 25 and 50 m levels. No major bias is expected in our results due to this approximation. On 13 November, the fog system exhibited a lower $[ANC]$ with respect to the previous night (see Fig. 7), but we did not observe any drastic change in the pH of fog water or in the total $[ACY]$, which coincided fairly well with $[Acy]_f$. A limited increase in $[ACY]$ was observed starting at 0800 in the morning, but the values remained negative. During the partial dissipation on 13 November, between 1200 and 1600, the ratio $[NO_3^-]/[SO_4^{2-}]$ remained close to 1, while on the previous day this ratio reached the value of 4 (see Subsection 3.4).

5.2. The titration approach

The trend of the total acidity of the system, from alkaline to acid and again to alkaline behaviour, over the time interval 0300–2300 on 12 November, can be viewed in terms of a titration, i.e., net acid addition followed by net addition of base (back-titration). By interpolation of the $[ACY]$ data for the period 0300–2300 on 12 November through a non-linear (cubic) regression (Fig. 8), the titration plots as a function of time are obtained for ground and 25 m levels. The 50 m plot is not reported since the few points available do not allow a good interpolation. Four key points are observed in the

plots of the function, which allow some further considerations on the system under examination:

- (1) minimum (MN)
- (2) 1st intercept point at $[ACY] = 0$ (E_1)
- (3) maximum (MX)
- (4) 2nd intercept point at $[ACY] = 0$ (E_2)

MN indicates the time when the net acid addition to the system initiated (ca. 0500 at 25 m, ca. 0600 at the ground). E_1 represents the time at which the added acid had consumed the entire $[ANC]$ of the system (ca. 1200 at 25 m, ca. 1400 at the ground), i.e., the system was no longer buffered with respect to acid addition. From this time on, all net acidity added to the system resulted in a corresponding addition of free acidity (see Fig. 7). The net addition of ca. 250 neq m^{-3} of acid in the time interval 0600–1100 caused a fog water pH variation from 5.6 to 4.5 (ca. $30 \mu\text{eq l}^{-1}$ difference in liquid phase acidity), while a further addition of ca. 300 neq m^{-3} caused a pH drop from 4.5 to 2.8 (difference of ca. $1500 \mu\text{eq l}^{-1}$). MX (between 1900 and 2000 at both levels) indicates the time at which the effect of the acid addition ended, and the back-titration process started, i.e., a basic component was added to the system at a rate that neutralized the net acidity present in the system itself. $[ACY]$ decreased and reached the second equivalence point (E_2) of the titration curve ($[ACY] = 0$) at ca. 2300 at both levels. It should be noted that the pH value corresponding to $[ACY] = 0$ (ca. 4.5) represents the pH of our fog water proton reference level (see Charlson and Rodhe (1982) for a discussion of the atmospheric significance of this value).

From the titration approach, it is also possible to derive a dynamic estimation of the input of net acidity that caused the observed drop in fog water pH. The calculation is straightforward: between 0600, when the net acid addition (titration) starts, and 1900, beginning of the back-titration, about 500 neq m^{-3} of net acidity are added to the system, which results in a mean addition rate of $40 \text{ neq m}^{-3} \text{ h}^{-1}$. This figure is not an absolute value, but represents the difference between the actual rate of base neutralizing species and acid neutralizing species added to the system. While it is evident that the neutralization of acidity is caused by NH_3 emissions within the system, some considerations are necessary to account for the input of acidic species.

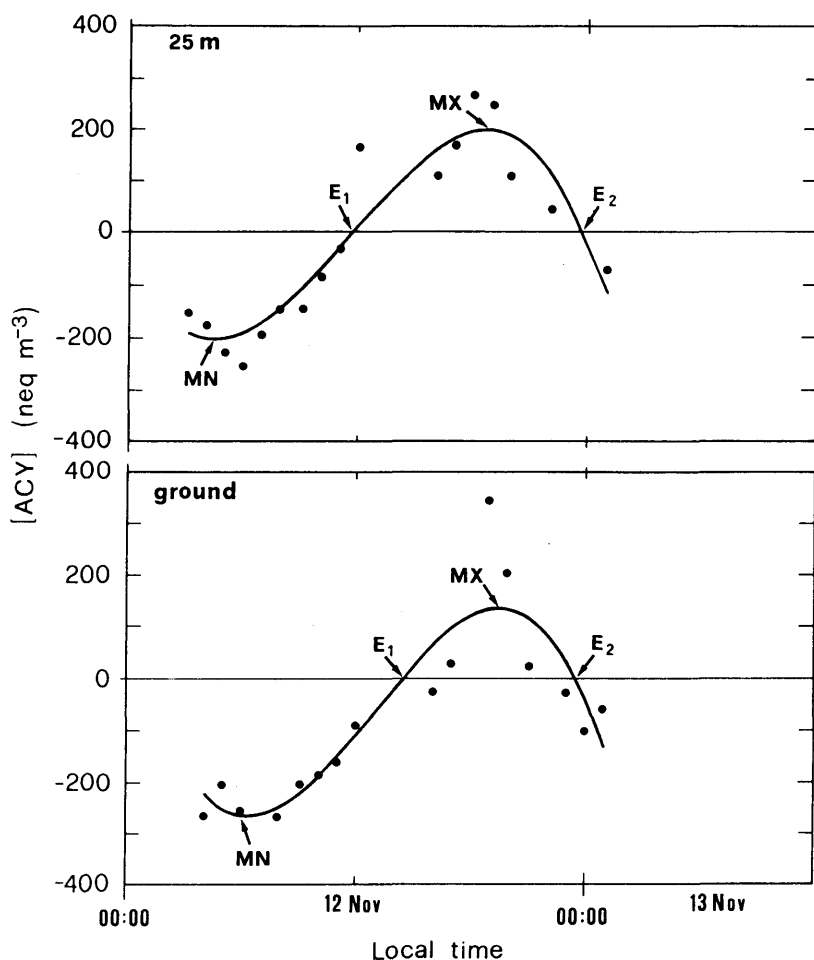


Fig. 8. Best fit, obtained with a cubic regression, of the temporal evolution at different heights of the calculated total atmospheric acidity ($[ACY]$), over the time interval 0300–2300 on 12 November. The 50 m plot is not reported since the few experimental data available over the reported time period did not allow a good interpolation. The plotted functions describe a titration/back-titration process, which is discussed in the text.

5.3. Possible explanations for the acid input to the system

From the previous discussion of the data collected during the experiment, it is clear that an input of strong acid caused the pH decrease on 12 November. The large increase reported above of $[NO_3^-]$ in the liquid phase with respect to $[SO_4^{2-}]$ also testifies that the strong acid was actually HNO_3 . Two possibilities exist to account for this HNO_3 input: in-situ production and/or transport. In evaluating these two different possi-

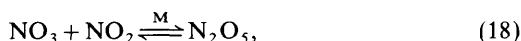
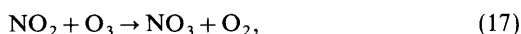
bilities we should take into account the differences in meteorology and chemical composition of the system between the day 12 November, when the acid input occurred, and the day 13 November during which no such input took place. This comparison is particularly useful, since our considerations on HNO_3 input are mostly based on indirect experimental evidence. This is particularly true since it is not possible to directly detect a gaseous HNO_3 input to the system, because in fog conditions HNO_3 immediately dissolves within the droplets.

HNO_3 can be photochemically produced during the day in the interstitial air by the reaction:



However, the measured UV-B radiation (280–315 nm) level is exactly the same on both days 12 and 13 November, with maximum values at 1200 of 1.5 and $2 \mu\text{W cm}^{-2}$, at the ground and 50 m, respectively. This of course does not tell us whether or not reaction (16) was effective in HNO_3 production within our system, but only that the HNO_3 production should be comparable on both days. Also, reaction (16) does not account for the initial acid production, which is observed at least from 0600, before sunrise.

A night-time source of HNO_3 is the NO_2 oxidation by O_3 to form NO_3 radical and N_2O_5 , which is incorporated within the droplets yielding HNO_3 (Heikes and Thompson, 1983):



The transformation process described by eqs. (17) to (19) is initiated by the oxidation of NO_2 by O_3 , which is the rate-limiting step of the process. The titration of the [ALK] of the system starts early in the morning of 12 November, when O_3 concentration is very low (a few nmol m^{-3} ; Fuzzi et al., 1992b) and certainly cannot account for the measured HNO_3 production. On the other hand, O_3 concentration is higher in the first hours of the following day. Nitrite was also detected in fog water samples during the night between 11 and 12 November, at concentration levels up to $130 \mu\text{eq l}^{-1}$, which considerably decreased toward sunrise (see Fig. 2). However, even if all nitrite were oxidized to HNO_3 (Damschen and Martin, 1983), this reaction could not account for the observed HNO_3 input in our system.

Gaseous HNO_3 could have been introduced into the system from a different air mass, either from above the fog top or by horizontal advection of air masses near the ground (within the fog layer). Wobrock et al. (1992) reported from sodar measurements, large oscillations of the fog upper boundary on 13 November, while fog height remained nearly constant throughout 12 November.

From this observation we argue that mixing at the fog top was not effective on 12 November, and cannot be the cause of HNO_3 input. The main difference between meteorological conditions for the two days 12 and 13 November is the strong wind shear observed within the fog layer on 12 November from ca. 0000 to 1200. At the same time a distinct change in the origin of air masses near the ground was observed (Wobrock et al., 1992). As the air masses reaching the measuring site early on 12 November had already covered a great distance (100–200 km) within the Po Valley, advection of HNO_3 -rich air can be hypothesized.

5.4. Considerations regarding S(IV) to S(VI) transformation in fog

In addition to the contribution of HNO_3 to the acidity of our system, the S(IV) to S(VI) oxidation reaction can also, in principle, constitute a further source of acidity. However, liquid phase S(IV) oxidation in our fog system is a process of minor importance, primarily due to the very low concentration of SO_2 and of oxidant species like O_3 and H_2O_2 over the period of the experiment (Fuzzi et al., 1992b). In addition, S(IV) in fog water is mainly bound as HMSA (Facchini et al., 1992). Fe and Mn catalyzed oxidation is still possible, since the total concentration (soluble + insoluble) of these two components in fog water ranges from 2 to $20 \mu\text{mol l}^{-1}$ for Fe and from 0.5 to $8 \mu\text{mol l}^{-1}$ for Mn (Fuzzi et al., 1992b). These concentrations of Fe and Mn allow a potential SO_2 oxidation rate of a few percent per hour (Martin, 1984). However, even if all SO_2 in solution were oxidized to SO_4^- , the resulting liquid phase concentration would account for a negligible fraction of the total SO_4^- concentration in solution. At these levels, it is very difficult to discriminate between a possible contribution of S(IV) oxidation and of the aerosol SO_4^- scavenging from the interstitial air to the total liquid phase $[\text{SO}_4^-]$.

6. Conclusion

The concept of atmospheric acidity is well suited to a quantitative description of the multiphase atmospheric system studied here, where the oxidation processes are not very effective, due to the limited availability of oxidants. The chemistry of the fog system mainly concerns the exchange of

acidic and basic components between different atmospheric reservoirs, and is largely controlled by the presence of NH_3 emitted at the ground and its partitioning between gas, fog droplets and interstitial aerosol.

The chemical evolution of the fog system described here (duration of 63 hours) as a function of height above the ground allows the following main conclusions.

(a) The system was not closed, and increases were observed in the total concentration (gas + interstitial aerosol + fog droplets) of chemical species, especially during daytime. The [ACY] approach described in this paper allows the input of new material into the system and the redistribution among the phases to be taken into account.

(b) At the onset of fog, the system had a net alkaline character. The [ANC] of the system was exhausted, however, by an input of strong acid (HNO_3) occurring during the first part of the fog episode. The pH decrease observed on 12 November (from 5.6 to 2.8) can be described in terms of titration of the fog system. A back-titration process was observed, starting in the evening of 12 November, which caused the system to become alkaline again. The effect of the titration/back-titration processes was a depletion of the gaseous NH_3 reservoir; in fact, after the end of the back-titration process, [ACY] of the system coincided with the fog water acidity until the end of the fog episode.

(c) At the beginning of the fog episode, the system exhibited a greater alkaline character at the ground, compared to the higher levels; this was due to the observed negative gradient with height of NH_3 gaseous concentration. During fog evolution, on the contrary, no major [ACY] difference with height was observed, and the system appeared to be homogeneous, at least in the first 50 m, where chemical measurements were performed.

(d) No evidence of in-situ production of

HNO_3 was observed. Analysis of meteorological data supports the hypothesis of horizontal advection as a likely source of HNO_3 on 12 November.

(e) Liquid phase SO_2 oxidation is a process of minor importance in determining SO_4^{2-} concentration within the fog multiphase system.

(f) At high R.H., the atmospheric aerosol may contain relatively large fractions of liquid water (Svenningsson et al., 1992), and therefore the particles should be regarded as liquid solutions of high ionic strength (Pilinis et al., 1989). However, the gas/wet aerosol interaction and the chemistry of wet aerosol particles cannot be accounted for by our experimental results, as discussed in Subsection 3.2. This subject is still poorly understood in literature and should be investigated in future studies.

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