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# Factors determining the formation of secondary inorganic aerosol: a case study in the Po Valley (Italy)

S. Squizzato<sup>1</sup>, M. Masiol<sup>1</sup>, A. Brunelli<sup>1</sup>, S. Pistollato<sup>2</sup>, E. Tarabotti<sup>2</sup>,  
G. Rampazzo<sup>1</sup>, and B. Pavoni<sup>1</sup>

<sup>1</sup>DAIS – Dipartimento di Scienze Ambientali, Informatica e Statistica, Università Ca' Foscari Venezia, Dorsoduro 2137, 30123 Venice, Italy

<sup>2</sup>Dipartimento Provinciale di Venezia, Agenzia Regionale per la Prevenzione e Protezione Ambientale del Veneto, Via Lissa 6, 30174 Mestre, Italy

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Correspondence to: B. Pavoni (brown@unive.it)

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## Abstract

Physicochemical properties of aerosol were investigated by analyzing the inorganic water soluble content in PM<sub>2.5</sub> samples collected in the eastern part of the Po Valley (Italy). In this area the EU limits for many air pollutants are frequently exceeded as a consequence of local sources and regional-scale transport of secondary inorganic aerosol precursors. Nine PM<sub>2.5</sub>-bound major inorganic ions (F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>) were monitored over one year in three sites categorized as semi-rural background, urban background and industrial. The acidic properties of the PM<sub>2.5</sub> were studied by applying the recently developed E-AIM thermodynamic model 4. The experimental data were also examined in relation to the levels of gaseous precursors of SIA (SO<sub>2</sub>, NO<sub>x</sub>, NO, NO<sub>2</sub>) and on the basis of some environmental conditions having an effect on the secondary aerosols generation processes. A chemometric procedure using cluster analysis on experimental [NH<sub>4</sub><sup>+</sup>]/[SO<sub>4</sub><sup>2-</sup>] molar ratio and NO<sub>3</sub><sup>-</sup> concentration has been applied to determine the conditions needed for ammonium nitrate formation in different chemical environments. Finally, some considerations on the secondary inorganic aerosol formation and the most relevant weather conditions concerning the sulfate-nitrate-ammonium system were also discussed. The methods used can be easily applied to other environments to evaluate the physicochemical characteristics of aerosols and the climatic conditions necessary for the formation of ammonium sulfate and ammonium nitrate aerosols.

## 1 Introduction

The particulate matter (PM) is a multi-component system, that includes materials in the solid or liquid states and enters the atmosphere from both natural and anthropogenic sources. It can play an important role in the Earth's radiation budget (Forster et al., 2007), dim the atmospheric visibility (Bäumer et al., 2008), be involved in acid deposition (Larssen et al., 2006), produce major threats to cultural heritage (Nava et al.,

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2010) and be linked with a variety of respiratory illnesses, cardiovascular problems and life-expectancy reduction (Pope et al., 2009). PM can be distinguished in primary, directly emitted from sources, and secondary, subsequently formed in the atmosphere from chemical processes involving a set of precursor gases. This latter fraction is mainly generated through a series of chemical reactions involving nitrogen oxides ( $\text{NO}_x$ ), sulfur dioxide ( $\text{SO}_2$ ), ammonia ( $\text{NH}_3$ ) and a large number of volatile organic compounds (VOCs), which may react with ozone ( $\text{O}_3$ ), hydroxyl radical ( $\cdot\text{OH}$ ) and other reactive molecules forming the secondary inorganic aerosol (SIA) and secondary organic aerosol (SOA).

Sulfate ( $\text{SO}_4^{2-}$ ), nitrate ( $\text{NO}_3^-$ ) and ammonium ( $\text{NH}_4^+$ ) are the main SIA components in PM mainly occurring as ammonium sulfate ( $(\text{NH}_4)_2\text{SO}_4$ ) and ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ), which are originated, respectively by the neutralization of sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and nitric acid ( $\text{HNO}_3$ ) with ammonia (Stockwell et al., 2003). The neutralization of sulfuric acid generally prevails on the neutralization of nitric acid (Seinfeld and Pandis, 2006), but the production of secondary sulfates and/or nitrates strongly depends on several chemical and micro-meteorological factors, such as the levels of gaseous precursors, the concentrations of atmospheric oxidants, the characteristics of preexisting aerosols, the air temperature and humidity (Baek et al., 2004; Pathak et al., 2009). In Europe, non marine sulfate and nitrate contribute for a large part to the mass of the fine particulate matter (with aerodynamic diameter less than  $2.5\ \mu\text{m}$ ,  $\text{PM}_{2.5}$ ), ranging from 11 % to 35 % and from 1 % to 24 %, respectively (Putaud et al., 2010) and may also play a key role in the aerosol acidity and its negative effects on human health, ecosystems and materials. In coastal areas, also sea salts, mainly composed of  $\text{Cl}^-$  and  $\text{Na}^+$ , can influence  $\text{PM}_{2.5}$  levels and acidity. In Europe, even in the cases about 95 % of the total mass of marine aerosols is in the coarse mode (Seinfeld and Pandis, 2006), sea salt in  $\text{PM}_{2.5}$  ranges from less than 1 % (in remote continental areas) to 11 % (in Atlantic zones) (Putaud et al., 2010).

Since the annual limit fixed by the European Union for  $\text{PM}_{2.5}$  ( $25\ \mu\text{g m}^{-3}$  to be met in 2015; EC, 2008) is not, or not yet, achieved in several sites (EEA, 2012), the secondary

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and marine components are of major importance for the abatement measures to have their effect. Moreover, the knowledge of the atmospheric conditions influencing the SIA formation appear very important for deciding policies at both local and regional scales.

Several studies have quantified SIA in Europe (e.g., Putaud et al., 2004; Querol et al., 2004; Lonati et al., 2008) and studied its dispersion (e.g., Schaap et al., 2004a; Renner and Wolke, 2010), also considering gaseous pollutants (Bencs et al., 2008) and environmental conditions (Arsene et al., 2010). However, scarce information is available about the aerosol acidity. Moreover, ammonium nitrate formation was usually investigated using chemical equilibrium models mainly addressed to understand the partitioning between the gas and aerosol phases (e.g., Ansari and Pandis, 1999; Dassios and Pandis, 1999; Ansari and Pandis, 2000; Stockwell et al., 2000).

In this study an approach is proposed which easily interprets aerosol formation processes and acidity properties, using chemical experimental data (ion and gaseous precursors concentrations), readily available meteorological information and a thermodynamic model. Data have been collected in the eastern part of the Po Valley, a very air polluted region of Europe, where the acidic properties of aerosol may have a serious impact on human health, environment and cultural heritage. The  $PM_{2.5}$  and its content in major inorganic ions were monitored in three sites of different typologies (urban background, industrial and semi-rural background) near Venice (Italy), in the middle of a costal lagoon, where  $PM_{2.5}$  levels frequently exceed the EU limits and heavy levels of SIA components and sea salts were observed (Prodi et al., 2009; Squizzato et al., 2012; Masiol et al., 2012). Experimental ion data were examined in relation to the levels of gaseous precursors of SIA ( $SO_2$ ,  $NO_x$ ,  $NO$ ,  $NO_2$ ) and considering some environmental conditions having effects on SIA generation processes. The aerosol acidity was also modeled using the recently released thermodynamic model E-AIM4. A chemometric procedure using experimental  $[NH_4^+]/[SO_4^{2-}]$  molar ratio and  $NO_3^-$  concentration has been tested to explain the environmental and chemical conditions favoring the ammonium nitrate formation. The SIA formation processes and the most relevant weather conditions affecting the sulfate-nitrate-ammonium system were also discussed. The

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proposed approach, even though developed for the study area can be easily tailored to other environments.

## 2 Study area

The historical city center of Venice, settled in the middle of a  $\sim 550 \text{ km}^2$ -wide coastal lagoon, intensely inhabited since the 15th century, is one of the major touristic destinations in Italy. At present, it suffers from numerous anthropogenic pressures including coastal erosion, sediment and water contamination, eutrophication, exploitation of biological resources and air pollution. The main local anthropogenic activities influencing air quality in the Venice area are linked to domestic heating from urban areas ( $\sim 270\,000$  inhabitants), emissions from the industrial zone of Porto Marghera including chemicals, metallurgical factories, oil-refineries, coal and gas power plants, traffic exhaust from a frequently congested road network, artistic glass-making factories in the Island of Murano, shipping emissions from public and private boats, industrial and passenger terminals and flying traffic from an international airport (Rampazzo et al., 2008a,b). Natural contributions add crustal, marine and biological materials. Recently, the importance of the regional-scale transports of pollutants from the Po Valley and the transboundary transports from Eastern and Central Europe were also evidenced and assessed (Masiol et al., 2010; Squizzato et al., 2012; Masiol et al., 2012).

The most recent emission inventory (2005) published by ISPRA (2012) for the Venice area has reported that in the study area the fossil fuel combustion in energy and transformation industries and transportation emit several  $\text{Ggyr}^{-1}$  of  $\text{SO}_x$  ( $\text{SO}_2 + \text{SO}_3$ ) and nitrogen oxides, i.e. the gaseous precursors of SIA.

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## 3 Materials and methods

### 3.1 Sampling sites

The sampling sites were selected to characterize different emissive scenarios (Fig. 1). A semi-rural coastal background site (SRC) upwind to main emission sources was set on a lighthouse on the Adriatic coastline. A second site was placed in a high density residential zone to be representative of an urban background (UBG). A third site was selected close to the main industrial area of Porto Marghera for being representative of industrial emissions (IND).

### 3.2 Analytical

A PM<sub>2.5</sub> sampling campaign was started in January 2009 and lasted one year. Samples were collected simultaneously in the three sites on 47 mm quartz fiber filters (Whatman QMA, GE Healthcare, USA) using low volume automatic samplers set according to EN 14907 standards (2.3 m<sup>3</sup> h<sup>-1</sup>). PM<sub>2.5</sub> masses were obtained by gravimetric determination on filters preconditioned at constant temperature (20 ± 5 °C) and humidity (RH 50 ± 5 %) for at least 48 h. After sampling, filters were stored at -20 °C in the dark until analyses to avoid contamination and losses of the most volatile compounds.

Four period representative of different seasons, weather conditions and emissions were selected: spring (37 days, March–April 2009), summer (36 days, June–July 2009), autumn (42 days, September–October 2009) and winter (41 days, December 2009–January 2010). These samples (150 for each sampling site, 445 in total) were prepared using ultrasonic-assisted dissolution in 15 ml ultrapure water (resistivity ≈ 18 MΩ cm) and then analyzed on a ion chromatographic system (Dionex DX500, USA) for quantifying nine major inorganic ions (F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>). Details of analytical procedures and instrumental setup are given elsewhere (Squizzato et al., 2012). Sea-salt sulfate (ssSO<sub>4</sub><sup>2-</sup>) and non sea-salt sulfate (nssSO<sub>4</sub><sup>2-</sup>) were

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indirectly calculated using the seawater ratio as:

$$\text{ssSO}_4^{2-} = 0.25 \cdot \text{Na}^+ \quad (1)$$

$$\text{nssSO}_4^{2-} = \text{SO}_4^{2-} - \text{ssSO}_4^{2-} \quad (2)$$

In UBG and IND sites, the main gaseous SIA precursors ( $\text{SO}_2$ ,  $\text{NO}_x$ ,  $\text{NO}$ ,  $\text{NO}_2$ ) were hourly measured by the local environmental protection agency (ARPAV) network. Ultraviolet fluorescence was used for  $\text{SO}_2$  (Model 43A, Thermo Electron Co., USA) and chemiluminescence for nitrogen oxides (Model 42C, Thermo Electron Co., USA), following the EN 14212 and EN 14211 standards, respectively.

### 3.3 Thermodynamic model

The aerosol acidity is one of the most important parameters influencing atmospheric chemistry and physics, and the determination of in-situ aerosol properties as acidity and water content is fundamental to investigate the aerosol acidity characteristics and the role of heterogeneous chemistry in nitrate formation (Pathak et al., 2009). Previous studies (Zhang et al., 2000; Pathak et al., 2004; Zhang et al., 2007; Pathak et al., 2009; Engelhart et al., 2011; Pathak et al., 2011) applied the Extended Aerosol Inorganic Model (E-AIM, <http://www.aim.env.uea.ac.uk/aim/aim.php>; Clegg et al., 1998) to simulate the in-situ acidity ( $[\text{H}^+]_{\text{ins}}$ ), the aerosol water content (AWC) and the activities of ionic species in aqueous aerosols and the solid- and liquid-phase compositions. In this study, we used the E-AIM model IV (E-AIM4) recently developed by Friese and Ebel (2010) for  $\text{H}^+ - \text{NH}_4^+ - \text{Na}^+ - \text{SO}_4^{2-} - \text{NO}_3^- - \text{Cl}^- - \text{H}_2\text{O}$  mixtures to simulate the acidity and thermodynamic properties of  $\text{PM}_{2.5}$ . The average ambient temperature, relative humidity, and average molar concentrations of total aerosol acidity ( $[\text{H}^+]_{\text{Total}}$ ) and experimental data were used as the input in E-AIM4 to obtain  $[\text{H}^+]_{\text{ins}}$  and the moles of chemical species in aqueous phase. In this study,  $[\text{H}^+]_{\text{Total}}$  was estimated using the ionic balance of the most relevant inorganic ionic species (Lippmann et al., 2000;

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Pathak et al., 2009), including sulfate, nitrate, chloride, ammonium and sodium:

$$[\text{H}]_{\text{Total}}^+ = 2 \cdot \text{SO}_4^{2-} + \text{NO}_3^- + \text{Cl}^- - (\text{NH}_4^+ + \text{Na}^+) \quad (3)$$

Samples characterized by total acidity equal or less than zero were not modeled. Starting from the model outputs, the in-situ pH of aerosols was estimated as:

$$\text{pH} = -\log(f\text{H}_{\text{aq}}^+ \cdot x\text{H}_{\text{aq}}^+) \quad (4)$$

where  $f$  is the activity coefficient on mole fraction basis and  $x$  is the mole fractions of aqueous particle phase  $\text{H}^+$  (Zhang et al., 2007).

### 3.4 Sampling possible artifacts

Under certain conditions of temperature and humidity some artifacts can occur on the filters related to the interaction between the particles collected, the interaction between gas and particles, the capture of gas by the filter and evaporation of volatile and semi-volatile substances. These interactions can alter the composition of the collected particles. Ammonium sulfate can be considered as a conservative species (i.e. not subject to adsorption or volatilization) whereas ammonium nitrate is a semi volatile species and exists in a reversible phase equilibrium with nitric acid in the gas phase. Hence, the concentrations of aerosol-nitrate can be affected by the evaporative loss of the semi-volatile ammonium nitrate (negative artifact) or adsorption of nitric acid gas during or after the sampling (positive artifact); however, nitrate volatilization generally dominates on adsorption (Schaap et al., 2004b; Vecchi et al., 2009).

Depending on the composition of the aerosol, the temperature and relative humidity, the sampling artifacts for the ammonium nitrate can become significant (Pathak et al., 2009). A study conducted in the Po Valley in different environmental conditions showed that the evaporative loss of aerosol nitrate from the quartz filters is a function of temperature. At temperatures exceeding 25 °C evaporation is almost complete, whereas retention is dominant at temperature less than 20 °C (Schaap et al., 2004b).

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In addition, experimental results presented by Vecchi et al. (2009) showed that negative artifacts due to nitrate volatilization from the filters were on average 22 % on quartz filters in summer and no or negligible losses were observed in winter.

In the present study quartz filters were used in all samplings to minimize artifacts. On the basis of the measured temperatures averaged over the 24 h, only some summer samples (95 of 445) could have undergone sampling artifacts. The evaporative loss of aerosol nitrate has been estimated following the empirical correlations proposed in Pathak and Chan (2005) and Pathak et al. (2009),  $H^+$  has been estimated using the ionic balance. For ammonium rich samples:

$$\text{Nitrate loss (\%)} = 30 \cdot \left[ \ln \left( \frac{[NH_4^+]}{[NO_3^-]} \right) - 1.2 \right] \quad (5)$$

and for ammonium poor samples:

$$\text{Nitrate loss (\%)} = 30 \cdot \left[ \ln \left( \frac{[H^+]}{[NO_3^-]} \right) - 1.2 \right] \quad (6)$$

On this basis, the average aerosol nitrate loss was  $26 \% \pm 7$  and  $20 \% \pm 6$  in ammonium rich and ammonium poor samples, respectively, in accordance with Vecchi et al. (2009).

## 4 Results and discussion

### 4.1 Seasonal variations of gases and ionic species in $PM_{2.5}$

Some statistics of analytical data are summarized in Table 1. The industrial site presents higher annual average concentrations of  $SO_x$ ,  $NO_x$  and NO (6, 82 and  $28 \mu\text{g m}^{-3}$ , respectively) than UBG (4, 75 and  $22 \mu\text{g m}^{-3}$ ). Conversely, higher annual average concentrations of  $NO_2$  were observed in UBG ( $44 \mu\text{g m}^{-3}$ ) than in IND

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( $38 \mu\text{g m}^{-3}$ ). The annual limit value fixed by the European Union ( $40 \mu\text{g m}^{-3}$ , EC, 2008) for  $\text{NO}_2$  was exceeded only in UBG. Nitrogen oxides showed typical seasonal trends depending on changes in photochemistry and in emission rates, i.e. higher levels during the coldest months. Differently, no significant variations were recorded for  $\text{SO}_2$ .

5 The  $\text{PM}_{2.5}$  annual average mass was  $33 \mu\text{g m}^{-3}$  for the two mainland sites (UBG, IND) and  $26 \mu\text{g m}^{-3}$  for SRC.  $\text{PM}_{2.5}$  concentrations were inversely correlated with air temperature, with higher levels during the cold period (Table 1). Comparing these results with other data (ARPAV, 2010a,b), available since 2008 for URB and IND, seasonal means have apparently dropped from January to October, and conversely increased in

10 November and December.  $\text{PM}_{2.5}$  was strongly correlated in the three sites with similar levels in UBG and IND. On an annual basis, the secondary inorganic aerosol (SIA) given as the sum of  $\text{nssSO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{NH}_4^+$  account for  $9.5 \mu\text{g m}^{-3}$  (27% of  $\text{PM}_{2.5}$  mass) in UBG,  $9.6 \mu\text{g m}^{-3}$  (28%) in IND and  $9.5 \mu\text{g m}^{-3}$  (36%) in SRC. Annually, other analyzed anions ( $\text{F}^-$  and  $\text{Cl}^-$ ) account for about  $0.3 \mu\text{g m}^{-3}$  (1%) of the  $\text{PM}_{2.5}$  mass,

15 whereas on average other cations (sum of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ) generally not exceed  $0.7 \mu\text{g m}^{-3}$ . The ionic balance (expressed as equivalents,  $\text{neq m}^{-3}$ ) is shown in Fig. 2 as the average annual distribution of inorganic ions. Sulfate, nitrate, and ammonium contributed for about 85% of the total inorganic ionic species mass in all the sites. Other anions and cations contributed for a minor fraction of the water-soluble species

20 (2 and 7%, respectively) in all sites.

## 4.2 Aerosol acidity

Acidic aerosol have been widely observed in the atmosphere and can lead to significant consequences for both human health and ecosystems. They tend to be more hygroscopic than the neutral ones, and this enhances their ability of reflecting light and acting as condensation nuclei in the formation of droplets and clouds and their influence on visibility and climate (Pathak et al., 2004; Zhang et al., 2007). Furthermore acidic surfaces on atmospheric aerosols lead to potentially multifold increases in the

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mass of secondary organic aerosol (SOA). Even small amounts of acid are capable of catalyzing heterogeneous reactions depending on the ratio between particle acidity and relative humidity (Jang et al., 2002).

Aerosol acidity depends on strong acid content, mainly sulfuric and nitric acids, whose precursors occur both in gas and aqueous phases. Aerosol acidity characteristics can be summarized as follows: (i) total acidity  $[H^+]_{Total}$ , representing the sum of strong acids ( $H_2SO_4$ ,  $HNO_3$ ) in the water extract; (ii) in-situ acidity  $[H^+]_{ins}$ , defined as the moles of free hydrogen ions in the aqueous phase of aerosols per unit of air volume ( $nmol m^{-3}$ ). The in-situ acidity of aerosols is an important parameter for describing atmospheric processes and the environmental impact of atmospheric aerosol (Seinfeld and Pandis, 2006), as it affects many of the acidity-dependent heterogeneous chemical processes on the aerosol surfaces, such as the oxidation of  $SO_2$ , the hydrolysis of  $N_2O_5$ , and the formation of organic aerosols (Pathak et al., 2009, and reference therein). Moreover the acidity ratio (Engelhart et al., 2011) or neutralization ratio (NR) (Bencs et al., 2008):

$$NR = \frac{[NH_4^+]}{[SO_4^{2-}] + [NO_3^-]} \quad (7)$$

was used to describe the aerosol acidity, expressing the degree of neutralization of sulfate and nitrate by ammonium. On an annual basis, ammonium neutralizes almost completely sulfates and nitrates.

Table 1 reports the mean values of aerosol acidity parameters (NR,  $[H^+]_{Total}$ ,  $[H^+]_{ins}$ , pH) in the three sites during the four periods studied. Most of samples present a neutralization ratio equal to or less than 1 except in winter, when in UBG and IND NR assumes a value greater than 1 revealing an excess of ammonium. The highest average values of  $[H^+]_{Total}$  and  $[H^+]_{ins}$  were recorded in spring and winter, whereas the pH had similar values in all seasons and sites. IND had the largest seasonal variation of acidity with pH values higher in the cold and lower in the warm periods. The in situ acidity ( $[H^+]_{ins}$ ) accounted for 19%, 18% and 12% of the strong acidity ( $[H^+]_{Total}$ ) in

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SRC, UBG and IND, respectively, as an annual average, whereas pH values ranging between 2.0 (IND summer) and 3.9 (IND spring) were observed.

In Table 2 summer data have been compared with those of Pathak et al. (2009). The study area is clearly less polluted respect to Chinese cities and the levels of  $[H^+]_{Total}$  and  $[H^+]_{ins}$  are much lower than those presented in aforementioned work. Nevertheless, the percentage of  $[H^+]_{ins}$  to  $[H^+]_{Total}$  is comparable to that observed in Lanzhou (11 %).

### 4.3 Ammonium nitrate formation

Ammonium nitrate is formed in presence of high ammonia and  $HNO_3$  concentrations, low temperature and high humidity (Stockwell et al., 2000; Salvador et al., 2004; Pathak et al., 2009). At low  $NH_3$  concentrations, the neutralization of acidic sulfate by ammonia is favored over the formation of ammonium nitrate, which involves a homogeneous reaction between ammonia and nitric acid.  $[NH_4^+]/[SO_4^{2-}]$  molar ratio is commonly used to define ammonium nitrate formation in different environmental and chemical conditions. Several studies (Pathak et al., 2004, 2009; Arsene et al., 2010; Huang et al., 2011) have reported an increase of nitrate concentration for  $[NH_4^+]/[SO_4^{2-}] > 1.5$ . In samples characterized by  $[NH_4^+]/[SO_4^{2-}] > 1.5$  ammonium stabilizes nitrate whereas at  $[NH_4^+]/[SO_4^{2-}] < 1.5$ , nitrate neutralization may depend on: (i) gas-phase reaction between  $HNO_3$  and sea-salt particles (e.g.  $NaCl + HNO_{3(g)} \rightarrow NaNO_3 + HCl_{(g)}$ ) or fine crustal particles (e.g.  $CaCO_3$ ); (ii) heterogeneous hydrolysis of  $N_2O_5$  during nighttime on pre-existing ammonium sulfate particles in high relative humidity conditions.

In this study, the  $[NH_4^+]/[nssSO_4^{2-}]$  ratio, which represents the limit for ammonium nitrate formation, was used to investigate the sulfate-nitrate-ammonium system and the subsequent SIA generation processes. A q-mode cluster analysis using the Ward's Hierarchical agglomerative clustering method and the squared Euclidean distance measure was applied on  $NO_3^-$  and  $[NH_4^+]/[nssSO_4^{2-}]$  ratio. Three groups of samples have been identified by applying a normalized  $(D_{link}/D_{max} \cdot 100)$  cut-off of

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25 %, which represents the similarity value. Concentrations of  $\text{PM}_{2.5}$ ,  $\text{NO}_3^-$ ,  $\text{nssSO}_4^{2-}$ ,  $[\text{NH}_4^+]/[\text{nssSO}_4^{2-}]$  and  $[\text{NO}_3^-]/[\text{nssSO}_4^{2-}]$  ratios were computed for each group (Table 3).

Group 1 ( $N = 297$ ) is composed of samples collected in spring ( $N = 51$ ), summer ( $N = 95$ ), autumn ( $N = 98$ ) and winter ( $N = 51$ ) characterized by low  $\text{PM}_{2.5}$  and  $\text{NO}_3^-$  levels. Sulfate presents higher concentration than  $\text{NO}_3^-$  and the ratio  $[\text{NO}_3^-]/[\text{nssSO}_4^{2-}]$  is about 1. These samples show  $[\text{NH}_4^+]/[\text{nssSO}_4^{2-}] \sim 2$  and about half of samples present a ratio less than 2, indicating a deficit of  $\text{NH}_4^+$ . This is probably the result of a more photochemically active atmosphere, characteristic of the warmer periods when an enhanced generation of oxidants (mainly  $\cdot\text{OH}$  and  $\text{O}_3$ ) occurs. Moreover high temperature and a reduced availability of  $\text{NH}_4^+$  do not favor the production of  $\text{NH}_4\text{NO}_3$ .

Groups 2 ( $N = 118$ ) and 3 ( $N = 30$ ) are mainly formed by spring and winter samples. With respect to group 1, group 2 presents similar  $\text{nssSO}_4^{2-}$  average concentrations but higher availability of  $\text{NH}_4^+$  and lower temperature that favor higher  $\text{NO}_3^-$  concentrations. Samples of group 3 show the highest  $\text{NO}_3^-$  concentrations and  $[\text{NO}_3^-]/[\text{nssSO}_4^{2-}]$  molar ratios despite the concentration of  $\text{nssSO}_4^{2-}$  and the  $[\text{NH}_4^+]/[\text{nssSO}_4^{2-}]$  molar ratio are similar to group 2.

This may be due to more favorable conditions for the formation of ammonium nitrate (low temperature and high relative humidity), to a greater availability of  $\text{HNO}_3$  from higher emissions of  $\text{NO}_x$  (peculiar in cold period) and/or a more oxidizing atmosphere which favors the formation of nitric acid from nitrogen oxides. On the basis of these results, it is possible to define the excess ammonium as:

$$\text{excess}[\text{NH}_4^+] = \left( \frac{[\text{NH}_4^+]}{[\text{nssSO}_4^{2-}]} - 2 \right) \cdot [\text{nssSO}_4^{2-}] \quad (8)$$

Nitrate concentration increases when  $\text{excessNH}_4^+$  presents a 1:1 ratio as shown in Fig. 3a. Furthermore, the  $[\text{NO}_3^-]/[\text{nssSO}_4^{2-}]$  molar ratio increases for  $[\text{NH}_4^+]/[\text{nssSO}_4^{2-}] > 2$  (Fig. 3b).

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#### 4.4 Sulfur and nitrogen oxidation ratios

The Sulfur oxidation ratio (SOR) and Nitrogen oxidation ratio (NOR) have been used to evaluate the degree of atmospheric conversion of  $\text{SO}_2$  to  $\text{nssSO}_4^{2-}$  and of  $\text{NO}_2$  to  $\text{NO}_3^-$  (e.g., Wang et al., 2005; Bencs et al., 2008; Gu et al., 2011), calculated as follows:

$$\text{SOR} = \frac{n - \text{nssSO}_4^{2-}}{n - \text{nssSO}_4^{2-} + n - \text{SO}_2} \quad (9)$$

$$\text{NOR} = \frac{n - \text{NO}_3^-}{n - \text{NO}_3^- + n - \text{NO}_2} \quad (10)$$

SOR values were higher than 0.1 both in UBG and IND (Table 1) showing that  $\text{SO}_2$  is photochemically oxidized in the atmosphere. The highest SOR values were observed during autumn and winter in IND. This may be due to specific sampling site characteristics (near a coal power plant characterized by sulfur emission) and to long range transport processes carrying secondary sulfates. The highest NOR values were observed in spring and winter due to favorable condition (low temperature and high relative humidity) for gas-to-particle conversion processes, in particular for ammonium nitrate formation. This is also confirmed by a negative correlation between temperature and NOR ( $r = -0.5$ ).  $\text{PM}_{2.5}$  concentrations are strongly correlated with  $\text{NO}_3^-$  ( $r = 0.9$ ),  $\text{NH}_4^+$  ( $r = 0.9$ ),  $\text{NO}_2$  ( $r = 0.7$ ) and NOR ( $r = 0.8$ ). Conversely, lower correlation ( $r < 0.5$ ) were observed between  $\text{PM}_{2.5}$ ,  $\text{nssSO}_4^{2-}$ ,  $\text{SO}_2$ ,  $\text{NH}_4^+$  and SOR and between SOR and temperature. On this basis, nitrate formation can occur at a local level, whereas  $\text{nssSO}_4^{2-}$  may depends on regional contributions.

With the aim of highlighting the relationship between PM, ions, gases and environmental conditions, a q-mode hierarchical cluster analysis (using Ward's agglomerative method and the squared Euclidean distance measures) was performed on a standardized (mean = 0; standard deviation = 1) dataset, including  $\text{PM}_{2.5}$ ,  $\text{NH}_4^+$ ,  $\text{nssSO}_4^{2-}$ ,  $\text{SO}_2$ , SOR,  $\text{NO}_3^-$ , NOR, temperature and relative humidity. Three groups of samples were

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5 extracted with similar characteristic (Table 4) and each group was subsequently interpreted according to wind speed and direction (Fig. 4), as described in Squizzato et al. (2012). Group 1 links most of the samples ( $N_{\text{UBG}} = 89$ ,  $N_{\text{IND}} = 76$ ) showing lower NOR values and concentration of PM, SIA ions and  $\text{NO}_2$  and higher temperatures than the other two groups. The wind rose is similar to that of the full period. In group 2 increase in concentrations of  $\text{PM}_{2.5}$ ,  $\text{NO}_3^-$ ,  $\text{nssSO}_4^{2-}$ ,  $\text{NH}_4^+$  and  $\text{NO}_2$  and also in NOR values is observed. As to the environmental conditions, group 2 presents lower temperature and higher relative humidity than group 1 and the wind rose shows a decreasing of the average wind speed. Group 3 identifies the heavy pollution events, combining samples characterized by the highest concentrations of all variables, lowest temperature and wind speed and high relative humidity. An increase of  $\text{NO}_2$  accounts for the increased  $\text{NO}_3^-$  concentration both in UBG and IND site. This relationship was not observed between  $\text{SO}_2$  and  $\text{nssSO}_4^{2-}$  in UBG. Conversely, in IND site increasing concentrations of  $\text{SO}_2$  correspond to an increase of sulfate.

15 In Squizzato et al. (2012), the local contribution of SIA was estimated. Seasonally, the highest local contributions were observed in spring and winter in particular for  $\text{PM}_{2.5}$ ,  $\text{NO}_3^-$  and  $\text{NH}_4^+$ , whereas the local shares of  $\text{nssSO}_4^{2-}$  are similar in different periods and were mainly attributed to regional transport processes. On this basis, nitrate formation can occur at local scale, enhanced by high availability of  $\text{NO}_2$  and conditions of low temperature and high relative humidity whereas  $\text{nssSO}_4^{2-}$  can be due to regional processes in UBG and also to local generation in IND. Heavy pollution events occur in correspondence of days characterized by atmospheric conditions with scarce ventilation that traps pollutants and low temperature, that favors SIA generation processes.

## 5 Conclusions

25 The formation of secondary inorganic particles and aerosol acidity in the atmosphere was studied by investigating the relationship between gaseous precursors and

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environmental conditions. The water soluble inorganic component represents a significant fraction of  $PM_{2.5}$ . In particular SIA accounts for  $9.5 \mu\text{g m}^{-3}$  (27 % of  $PM_{2.5}$  mass) in UBG,  $9.6 \mu\text{g m}^{-3}$  (28 %) in IND and  $9.5 \mu\text{g m}^{-3}$  (36 %) in SRC. Collected particles are acidic, in particular in spring and winter, with low pH values.

Nitrate concentrations increase for  $[\text{NH}_4^+]/[\text{nssSO}_4^{2-}] > 2$  and the excess ammonium, defined as  $\text{excess}[\text{NH}_4^+] = (([\text{NH}_4^+]/[\text{nssSO}_4^{2-}] - 2) \cdot [\text{nssSO}_4^{2-}])$  was in the 1:1 ratio with nitrate. The highest nitrate concentrations were observed during the cold period due to more favorable conditions for the formation of ammonium nitrate (low temperature and high relative humidity), to a greater availability of  $\text{HNO}_3$  from higher emissions of  $\text{NO}_x$  (peculiar in cold period) and/or a more oxidizing atmosphere favoring the formation of nitric acid from nitrogen oxides. In these conditions, also the highest NOR values were observed and  $PM_{2.5}$ ,  $\text{NO}_3^-$  and  $\text{NO}_2$  values were strongly correlated. On this basis it is apparent that nitrate formation can occur at local scale, enhanced by high availability of  $\text{NO}_2$  and conditions of low temperature and high relative humidity, whereas  $\text{nssSO}_4^{2-}$  is mainly transported by regional processes. High pollution events are the result of the concomitant occurrence of low-mobility atmospheric conditions, that tend to trap pollutants, and low temperature that enhances SIA generation processes. The proposed approach can be a useful tool to better understand the aerosol dynamics and it is easily adaptable to other atmospheric environments.

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**Table 1.** Descriptive statistics (mean  $\pm$  standard deviation) of experimental data (gases, ions, weather parameters), neutralization ratio,  $[H^+]_{Total}$ , E-AIM4 results ( $[H^+]_{ins}$ , pH) and oxidation ratios (SOR and NOR).

N		Spring			Summer		
		SRC 37	UBG 37	IND 30	SRC 36	UBG 36	IND 31
PM <sub>2.5</sub>	$\mu\text{g m}^{-3}$	26.8 $\pm$ 22.1	36.8 $\pm$ 31.3	32.0 $\pm$ 17.7	11.2 $\pm$ 4.7	14.5 $\pm$ 4.8	17.9 $\pm$ 14.2
SO <sub>4</sub> <sup>2-</sup>	$\mu\text{g m}^{-3}$	2.4 $\pm$ 1.3	2.4 $\pm$ 1.8	2.4 $\pm$ 1.0	2.7 $\pm$ 1.5	2.7 $\pm$ 1.6	3.4 $\pm$ 3.7
ssSO <sub>4</sub> <sup>2-</sup>	$\mu\text{g m}^{-3}$	0.05 $\pm$ 0.03	0.07 $\pm$ 0.07	0.13 $\pm$ 0.11	0.03 $\pm$ 0.02	0.07 $\pm$ 0.08	0.07 $\pm$ 0.05
nssSO <sub>4</sub> <sup>2-</sup>	$\mu\text{g m}^{-3}$	2.3 $\pm$ 1.3	2.3 $\pm$ 1.8	2.3 $\pm$ 1.0	2.7 $\pm$ 1.5	2.6 $\pm$ 1.6	3.7 $\pm$ 3.7
NO <sub>3</sub> <sup>-</sup>	$\mu\text{g m}^{-3}$	5.8 $\pm$ 6.4	6.4 $\pm$ 8.3	5.4 $\pm$ 4.2	0.9 $\pm$ 0.7	0.5 $\pm$ 0.5	0.7 $\pm$ 0.8
NH <sub>4</sub> <sup>+</sup>	$\mu\text{g m}^{-3}$	2.2 $\pm$ 2.0	2.4 $\pm$ 2.8	2.3 $\pm$ 1.3	1.1 $\pm$ 0.7	1.0 $\pm$ 0.6	0.9 $\pm$ 0.5
SIA	$\mu\text{g m}^{-3}$	10.2 $\pm$ 9.5	11.1 $\pm$ 12.6	10.0 $\pm$ 5.9	4.6 $\pm$ 2.3	4.1 $\pm$ 2.2	4.9 $\pm$ 4.5
SIA/PM <sub>2.5</sub>	%	36.3 $\pm$ 5.7	26.4 $\pm$ 8.6	31.7 $\pm$ 8.7	41.5 $\pm$ 10.7	26.4 $\pm$ 7.5	26.1 $\pm$ 6.1
SO <sub>2</sub>	$\mu\text{g m}^{-3}$	–	4.6 $\pm$ 3.2	6.6 $\pm$ 4.0	–	5.3 $\pm$ 3.8	5.0 $\pm$ 3.2
NO	$\mu\text{g m}^{-3}$	–	20.5 $\pm$ 20.6	27.5 $\pm$ 23.7	–	3.4 $\pm$ 3.4	7.4 $\pm$ 4.7
NO <sub>2</sub>	$\mu\text{g m}^{-3}$	–	48.1 $\pm$ 15.4	34.6 $\pm$ 11.5	–	36.1 $\pm$ 9.3	29.4 $\pm$ 6.3
NO <sub>x</sub>	$\mu\text{g m}^{-3}$	–	73.1 $\pm$ 44.6	76.9 $\pm$ 46.8	–	32.0 $\pm$ 13.4	40.7 $\pm$ 12.2
T	$^{\circ}\text{C}$	9.0 $\pm$ 2.2	10.5 $\pm$ 2.2	10.8 $\pm$ 2.2	22.6 $\pm$ 2.1	24.6 $\pm$ 2.2	24.2 $\pm$ 2.2
RH	%	82.2 $\pm$ 13.7	78.7 $\pm$ 13.5	76.0 $\pm$ 13.4	79.0 $\pm$ 7.8	74.7 $\pm$ 6.0	74.9 $\pm$ 6.1
NR	–	0.8 $\pm$ 0.2	0.8 $\pm$ 0.2	0.9 $\pm$ 0.2	0.8 $\pm$ 0.2	0.8 $\pm$ 0.1	0.7 $\pm$ 0.3
SOR	–	–	0.28 $\pm$ 0.16	0.22 $\pm$ 0.09	–	0.28 $\pm$ 0.13	0.31 $\pm$ 0.20
NOR	–	–	0.07 $\pm$ 0.07	0.10 $\pm$ 0.05	–	0.01 $\pm$ 0.01	0.02 $\pm$ 0.02
N		29	26	18	30	20	19
$[H^+]_{Total}$	$\text{nmol m}^{-3}$	28.7 $\pm$ 26.9	22.1 $\pm$ 25.2	19.5 $\pm$ 21.0	9.4 $\pm$ 6.3	7.8 $\pm$ 6.0	12.1 $\pm$ 10.7
$[H^+]_{ins}$	$\text{nmol m}^{-3}$	6.1 $\pm$ 12.2	2.9 $\pm$ 4.7	0.2 $\pm$ 0.1	1.2 $\pm$ 1.1	1.2 $\pm$ 1.0	2.0 $\pm$ 1.7
pH	–	3.4 $\pm$ 0.7	3.6 $\pm$ 0.4	3.9 $\pm$ 0.1	2.5 $\pm$ 0.7	2.3 $\pm$ 0.5	2.0 $\pm$ 0.5

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Table 1. Continued.

N		Autumn			Winter		
		SRC 40	UBG 38	IND 42	SRC 41	UBG 38	IND 41
PM <sub>2.5</sub>	µgm <sup>-3</sup>	26.0 ± 18.2	29.6 ± 16.2	29.5 ± 14.9	38.8 ± 15.7	50.6 ± 21.4	49.3 ± 20.3
SO <sub>4</sub> <sup>2-</sup>	µgm <sup>-3</sup>	4.6 ± 3.6	4.3 ± 3.2	4.4 ± 3.4	4.1 ± 2.9	3.8 ± 2.6	3.9 ± 2.3
ssSO <sub>4</sub> <sup>2-</sup>	µgm <sup>-3</sup>	0.11 ± 0.08	0.04 ± 0.01	0.03 ± 0.01	0.05 ± 0.05	0.04 ± 0.02	0.03 ± 0.01
nssSO <sub>4</sub> <sup>2-</sup>	µgm <sup>-3</sup>	4.5 ± 3.6	4.3 ± 3.2	4.4 ± 3.4	4.1 ± 2.9	3.8 ± 2.6	3.9 ± 2.3
NO <sub>3</sub> <sup>-</sup>	µgm <sup>-3</sup>	3.5 ± 5.1	2.9 ± 4.5	2.7 ± 3.9	5.2 ± 3.4	6.1 ± 3.9	5.7 ± 3.6
NH <sub>4</sub> <sup>+</sup>	µgm <sup>-3</sup>	2.6 ± 2.2	2.4 ± 2.0	2.3 ± 1.9	2.9 ± 1.7	3.3 ± 1.6	3.4 ± 1.6
SIA	µgm <sup>-3</sup>	10.6 ± 9.1	9.6 ± 8.1	9.4 ± 7.5	12.2 ± 6.7	13.1 ± 7.0	12.9 ± 6.4
SIA/PM <sub>2.5</sub>	%	36.1 ± 10.3	28.3 ± 11.6	28.5 ± 12.0	30.3 ± 9.3	25.8 ± 7.7	26.6 ± 8.1
SO <sub>2</sub>	µgm <sup>-3</sup>	–	2.1 ± 2.3	5.6 ± 5.3	–	3.5 ± 2.1	5.5 ± 4.1
NO	µgm <sup>-3</sup>	–	19.9 ± 21.4	28.0 ± 24.2	–	35.0 ± 23.1	46.1 ± 31.0
NO <sub>2</sub>	µgm <sup>-3</sup>	–	41.6 ± 10.0	38.1 ± 8.5	–	47.6 ± 12.4	47.2 ± 10.8
NO <sub>x</sub>	µgm <sup>-3</sup>	–	19.9 ± 21.4	81.0 ± 42.7	–	35.0 ± 23.1	117.9 ± 55.3
T	°C	16.6 ± 4.3	17.6 ± 4.0	17.0 ± 4.3	3.3 ± 2.5	3.7 ± 2.4	3.7 ± 2.6
RH	%	79.4 ± 12.7	77.1 ± 11.7	76.4 ± 11.4	88.9 ± 10.4	85.5 ± 10.8	85.3 ± 10.9
NR	–	0.9 ± 0.2	0.9 ± 0.2	0.9 ± 0.2	0.9 ± 0.2	1.1 ± 0.2	1.1 ± 0.1
SOR	–	–	0.62 ± 0.25	0.35 ± 0.23	–	0.41 ± 0.19	0.38 ± 0.19
NOR	–	–	0.04 ± 0.05	0.05 ± 0.06	–	0.08 ± 0.04	0.08 ± 0.04
N		15	19	28	34	14	15
[H <sup>+</sup> ] <sub>Total</sub>	nmolm <sup>-3</sup>	8.2 ± 3.8	5.6 ± 3.8	10.9 ± 14.3	18.7 ± 11.6	36.0 ± 50.8	11.5 ± 13.8
[H <sup>+</sup> ] <sub>Ins</sub>	nmolm <sup>-3</sup>	1.8 ± 1.0	0.9 ± 0.6	2.3 ± 5.2	3.5 ± 5.9	8.0 ± 17.4	1.9 ± 4.6
pH	–	3.2 ± 0.9	3.1 ± 0.6	2.7 ± 0.7	3.6 ± 0.3	3.5 ± 0.5	3.8 ± 0.3

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**Table 2.** Comparison of aerosol acidity between data observed in this study and in Pathak et al. (2009).

Site Period		SRC	UBG	IND	Beijing Summer	Shanghai	Lanzhou	Guangzhou
[H <sup>+</sup> ] <sub>Total</sub>	nmol m <sup>-3</sup>	9.4 ± 6.3	7.8 ± 6.0	12.1 ± 10.7	390 ± 545	220 ± 225	65 ± 44	70 ± 58
[H <sup>+</sup> ] <sub>Ins</sub>	nmol m <sup>-3</sup>	1.2 ± 1.1	1.2 ± 1.0	2.0 ± 1.7	228 ± 344	96 ± 136	7 ± 6	25 ± 29
pH	–	2.5 ± 0.7	2.3 ± 0.5	2.0 ± 0.5	–0.52 ± 0.62	–0.77 ± 0.67	–0.38 ± 0.64	0.61 ± 0.71

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**Table 3.** Mean and standard deviation for  $\text{PM}_{2.5}$  ( $\mu\text{g m}^{-3}$ ),  $\text{NO}_3^-$  ( $\mu\text{g m}^{-3}$ ),  $\text{nssSO}_4^{2-}$  ( $\mu\text{g m}^{-3}$ ) and molar ratios  $[\text{NH}_4^+]/[\text{nssSO}_4^{2-}]$  and  $[\text{NO}_3^-]/[\text{nssSO}_4^{2-}]$ .

Group	$\text{PM}_{2.5}$	$\text{NO}_3^-$	$\text{nssSO}_4^{2-}$	$\frac{[\text{NH}_4^+]}{[\text{nssSO}_4^{2-}]}$	$\frac{[\text{NO}_3^-]}{[\text{nssSO}_4^{2-}]}$
1	$22 \pm 13$	$2 \pm 2$	$3 \pm 3$	$2 \pm 1$	$1 \pm 1$
2	$43 \pm 18$	$6 \pm 2$	$3 \pm 2$	$7 \pm 2$	$4 \pm 2$
3	$82 \pm 24$	$18 \pm 5$	$5 \pm 2$	$7 \pm 2$	$6 \pm 2$

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**Table 4.** Average values for each group identified by qHCA analysis.

	<i>N</i>	PM <sub>2.5</sub>	NH <sub>4</sub> <sup>+</sup>	nssSO <sub>4</sub> <sup>2-</sup>	SO <sub>2</sub>	SOR	NO <sub>3</sub> <sup>-</sup>	NO <sub>2</sub>	NOR	<i>T</i>	RH
<b>UBG</b>											
All	139	34.5	2.4	3.3	3.7	0.4	4.2	43.9	0.05	13.2	79.5
Group 1	89	21.1	1.2	1.9	3.8	0.3	2	39.9	0.03	14.7	77.3
Group 2	38	48.2	3.6	5.9	3.2	0.6	4.5	47.2	0.06	11.2	81.6
Group 3	12	90.1	7.4	5.8	5	0.5	20.3	63.5	0.19	8.7	88.5
<b>IND</b>											
All	145	33.1	2.3	3.6	5.6	0.3	3.7	38.1	0.06	13.5	78.6
Group 1	76	21.9	1.2	3.4	6	0.3	1.1	33.7	0.02	18.8	72.6
Group 2	36	32.4	2.2	2.3	3.9	0.3	4.5	36.9	0.08	8.6	87.2
Group 3	33	59.7	4.7	5.4	6.7	0.5	8.7	49.2	0.12	6.6	82.9

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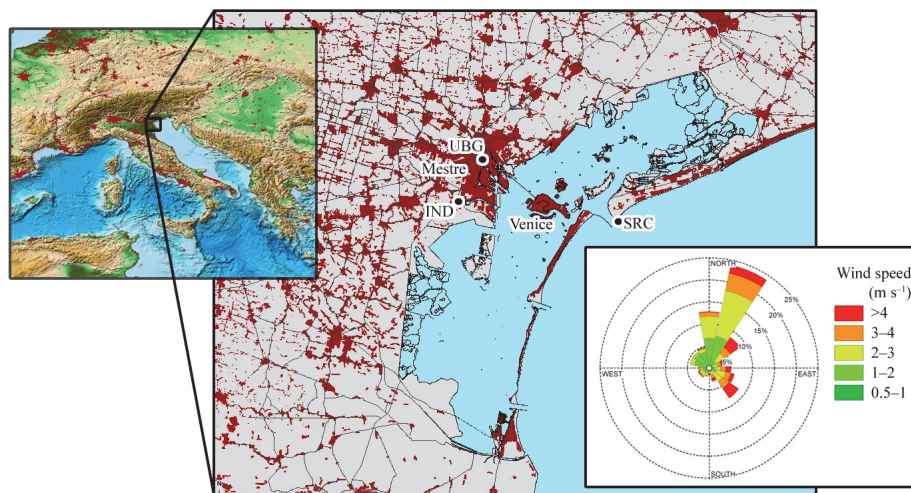
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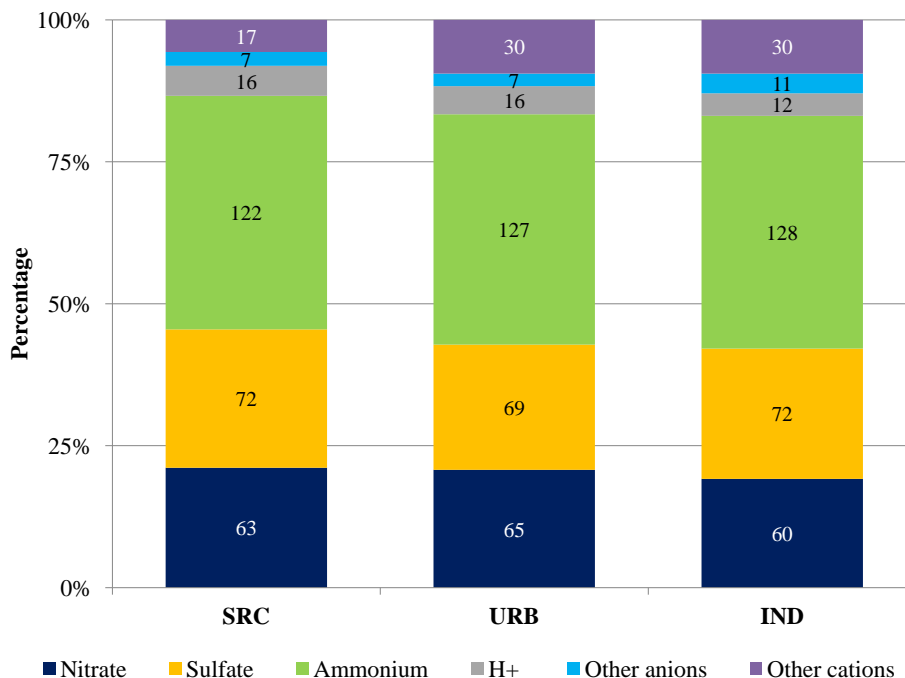


**Fig. 1.** Study area and wind rose computed for the 2009. The main urban settlements are red colored.

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**Fig. 2.** Annually average distribution of water soluble inorganic ions on  $PM_{2.5}$ . Number inside the bars represent the average concentration express in  $neq m^{-3}$ .

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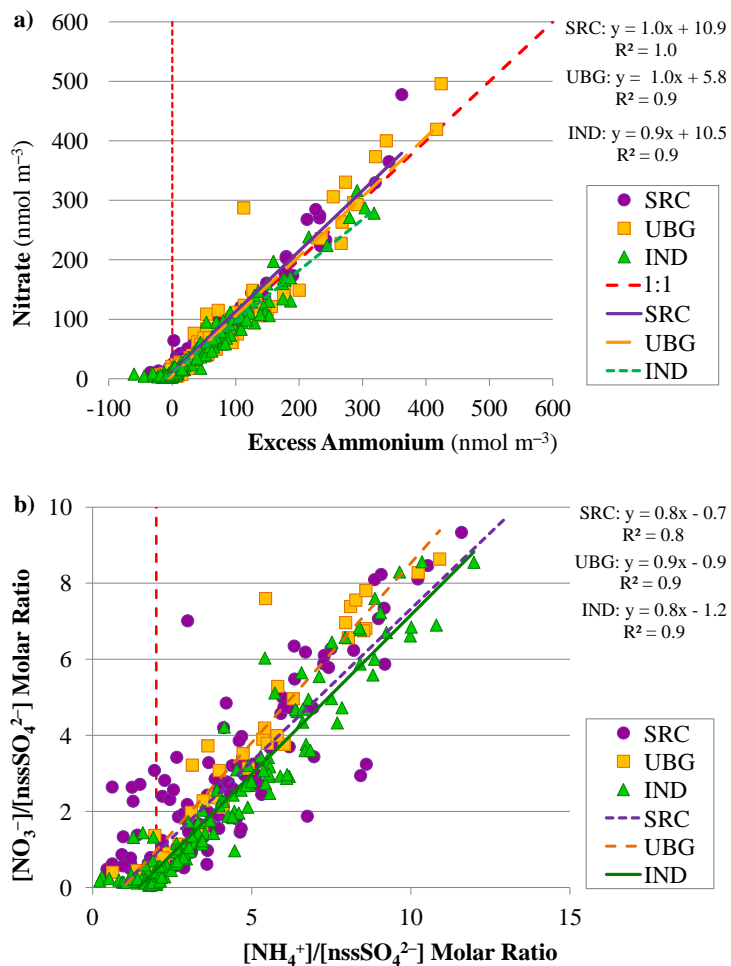
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**Fig. 3.** Nitrate concentrations as a function of excess ammonium (a) and nitrate-to-sulfate molar ratio as a function of ammonium-to-sulfate molar ratio (b).

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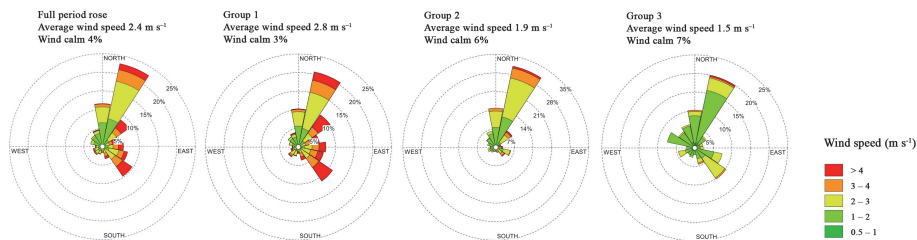
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**Fig. 4.** Wind rose computed for each group identified by qHCA for UBG site.

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