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

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Abstract

Physicochemical properties of aerosol were investigated by analyzing the inorganic water soluble content in PM_{2.5} 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_{2.5}-bound major inorganic ions (F⁻, Cl⁻, NO₃⁻, SO₄²⁻, Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺) were monitored over one year in three sites categorized as semi-rural background, urban background and industrial. The acidic properties of the PM_{2.5} were studied by applying the recently developed E-AIM thermodynamic model. The experimental data were also examined in relation to the levels of gaseous precursors of SIA (SO₂, NO_x, NO, NO₂) 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 [NH₄⁺]/[SO₄²⁻] molar ratio and NO₃⁻ 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 (NO_x), sulfur dioxide (SO_2), ammonia (NH_3) and a large number of volatile organic compounds (VOCs), which may react with ozone (O_3), hydroxyl radical ($\cdot\text{OH}$) and other reactive molecules forming the secondary inorganic aerosol (SIA) and secondary organic aerosol (SOA).

Sulfate (SO_4^{2-}), nitrate (NO_3^-) and ammonium (NH_4^+) are the main SIA components in PM mainly occurring as ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) and ammonium nitrate (NH_4NO_3), which are originated, respectively by the neutralization of sulfuric acid (H_2SO_4) and nitric acid (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 Cl^- and 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 $\text{PM}_{2.5}$ 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 coastal lagoon, where $\text{PM}_{2.5}$ 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 $[\text{NH}_4^+]/[\text{SO}_4^{2-}]$ 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 Ggyr^{-1} of 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 $\text{PM}_{2.5}$ 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 ($2.3 \text{ m}^3 \text{ h}^{-1}$). $\text{PM}_{2.5}$ masses were obtained by gravimetric determination on filters preconditioned at constant temperature ($20 \pm 5 \text{ }^\circ\text{C}$) and humidity (RH $50 \pm 5 \%$) for at least 48 h. After sampling, filters were stored at $-20 \text{ }^\circ\text{C}$ 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 $\approx 18 \text{ M}\Omega \text{ cm}$) and then analyzed on a ion chromatographic system (Dionex DX500, USA) for quantifying nine major inorganic ions (F^- , Cl^- , NO_3^- , SO_4^{2-} , Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+}). Details of analytical procedures and instrumental setup are given elsewhere (Squizzato et al., 2012). Sea-salt sulfate (ssSO_4^{2-}) and non sea-salt sulfate (nssSO_4^{2-}) were

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indirectly calculated using the seawater ratio as:

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

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

5 In UBG and IND sites, the main gaseous SIA precursors (SO_2 , NO_x , NO , NO_2) were hourly measured by the local environmental protection agency (ARPAV) network. Ultraviolet fluorescence was used for 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.

10 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:

$$5 \text{ pH} = -\log(f\text{H}_{\text{aq}}^+ \cdot x\text{H}_{\text{aq}}^+) \quad (4)$$

where f is the activity coefficient on mole fraction basis and x is the mole fractions of aqueous particle phase 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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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 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 $\text{PM}_{2.5}$, NO_3^- , nssSO_4^{2-} , NH_4^+ and 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 NO_2 accounts for the increased NO_3^- concentration both in UBG and IND site. This relationship was not observed between SO_2 and nssSO_4^{2-} in UBG. Conversely, in IND site increasing concentrations of SO_2 correspond to an increase of sulfate.

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 $\text{PM}_{2.5}$, NO_3^- and NH_4^+ , whereas the local shares of 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 NO_2 and conditions of low temperature and high relative humidity whereas 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

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 $\text{PM}_{2.5}$. In particular SIA accounts 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. 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 HNO_3 from higher emissions of 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 $\text{PM}_{2.5}$, NO_3^- and 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 NO_2 and conditions of low temperature and high relative humidity, whereas 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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References

ARPAV (Environmental Protection Agency of Veneto Region): The quality of the air in the municipality of Venice, ARPAV annual report 2009, 113, available online: <http://www.comune.>

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- venezia.it/flex/cm/pages/ServeBLOB.php/L/IT/IDPagina/29764, 2010a, last access: 31 January 2012. 16386
- ARPAV (Environmental Protection Agency of Veneto Region): Regional relation of air quality, ARPAV report 2009, 59 pp., available online: http://www.arpa.veneto.it/Download/Relazione_regionale_aria_2009.pdf, 2010b, last access: 31 January 2012. 16386
- 5 Arsene, C., Olariu, R. I., Zarmas, P., Kanakidou, M., and Mihalopoulos, N.: Ion composition of coarse and fine particles in Iasi, North-Eastern Romania: implications for aerosols chemistry in the area, *Atmos. Environ.*, 45, 906–911, 2010. 16380, 16388
- Ansari, A. S. and Pandis, S. N.: Prediction of multicomponent inorganic atmospheric aerosol behavior, *Atmos. Environ.*, 33, 745–757, 1999. 16380
- 10 Ansari, A. S. and Pandis, S. N.: The effect of metastable equilibrium states on the partitioning of nitrate between the gas and aerosol phases, *Atmos. Environ.*, 34, 157–168, 2000. 16380
- Baek, B. H., Aneja, V. P., and Tong, Q.: Chemical coupling between ammonia, acid gases, and fine particles, *Environ. Pollut.*, 129, 89–98, 2004. 16379
- 15 Bäumer, D., Vogel, B., Versick, S., Rinke, R., Möhler, O., and Schnaiter, M.: Relationship of visibility, aerosol optical thickness and aerosol size distribution in an ageing air mass over South-West Germany, *Atmos. Environ.*, 42, 989–998, 2008. 16378
- Bencs, L., Ravindra, K., de Hoog, J., Rasoazanany, E. O., Deutsch, F., Bleux, N., Berghmans, P., Roekens, E., Krata, A., and Van Grieken, R.: Mass and ionic composition of atmospheric fine particles over Belgium and their relation with gaseous air pollutant, *J. Environ. Monit.*, 10, 1148–1157, 2008. 16380, 16387, 16390
- 20 Clegg, S. L., Brimblecombe, P., and Wexler, A. S.: A thermodynamic model of the system $\text{H}^+ - \text{NH}_4^+ - \text{SO}_4^{2-} - \text{NO}_3^- - \text{H}_2\text{O}$ at tropospheric temperatures, *J. Phys. Chem. A*, 102, 2137–2154, 1998. 16383
- 25 Dassios, K. G. and Pandis, S. N.: The mass accommodation coefficient of ammonium nitrate aerosol, *Atmos. Environ.*, 33, 2993–3003, 1999. 16380
- EC (European Commission): Council Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe, *Official J. Eur. Commun.*, L152/1, 2008. 16379, 16386
- 30 EEA (European Environment Agency) AirBase – The European air quality database: available online: <http://www.eea.europa.eu/themes/air/airbase>, last access: 31 January 2012. 16379

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- Engelhart, G. J., Hildebrandt, L., Kostenidou, E., Mihalopoulos, N., Donahue, N. M., and Pandis, S. N.: Water content of aged aerosol, *Atmos. Chem. Phys.*, 11, 911–920, doi:10.5194/acp-11-911-2011, 2011. 16383, 16387
- 5 Forster, P., Ramaswamy, V., Artaxo, P., Berntsen, T., Betts, R., Fahey, D. W., Haywood, J., Lean, J., Lowe, D. C., Myhre, G., Nganga, J., Prinn, R., Raga, G., Schulz, M., and Van Dorland, R.: Changes in atmospheric constituents and in radiative forcing, in: *Climate Change 2007: The Physical Science Basis, Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*, edited by: Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K. B., Tignor, M., and Miller, H. L., Cambridge University Press, Cambridge, UK, and New York, USA, 2007. 16378
- 10 Friese, E. and Ebel, A.: Temperature dependent thermodynamic model of the system $\text{H}^+ - \text{NH}_4^+ - \text{Na}^+ - \text{SO}_4^{2-} - \text{NO}_3^- - \text{Cl}^- - \text{H}_2\text{O}$, *J. Phys. Chem. A*, 114, 11595–11631, 2010. 16383
- Gu, J., Bai, Z., Li, W., Wu, L., Liu, A., Dong, H., and Xie, Y.: Chemical composition of $\text{PM}_{2.5}$ during winter in Tianjin, China, *Particuology*, 9, 215–221, 2011. 16390
- 15 Huang, X., Qiu, R., Chan, C. K., and Pathak, R. K.: Evidence of high $\text{PM}_{2.5}$ strong acidity in ammonia-rich atmosphere of Guangzhou, China: Transition in pathways of ambient ammonia to form aerosol ammonium at $[\text{NH}_4^+]/[\text{SO}_4^{2-}] = 1.5$, *Atmos. Res.*, 99, 488–495, 2011. 16388
- ISPRA (Italian Institute for Environmental Protection and Research) disaggregated emission inventory 2005: available online: http://www.sinanet.isprambiente.it/it/inventaria/disaggregazione_prov2005/, last access: 1 March 2012. 16381
- 20 Jang, M., Czoschke, N. M., Lee, S., and Kamens, R. M.: Heterogeneous atmospheric aerosol production by acid catalyzed particle-phase reactions, *Science*, 298, 814–817, 2002. 16387
- Larssen, T., Lydersen, E., Tang, D. G., He, Y., Gao, J. X., Liu, H. Y., Duan, L., Seip, H. M., Vogt, R. D., Mulder, J., Shao, M., Wang, Y. H., Shang, H., Zhang, X. S., Solberg, S., Aas, W., Okland, T., Eilertsen, O., Angell, V., Liu, Q. R., Zhao, D. W., Xiang, R. J., Xiao, J. S., and Luo, J. H.: Acid rain in China, *Environ. Sci. Technol.*, 40, 418–425, 2006. 16378
- 25 Lippmann, M., Xiong, J. Q., and Li, W.: Development of a continuous monitoring system for PM_{10} and components of $\text{PM}_{2.5}$, *Appl. Occupat. Environ. Hyg.*, 15, 57–67, 2000. 16383
- Lonati, G., Giugliano, M., and Ozgen, S.: Primary and secondary components of $\text{PM}_{2.5}$ in Milan (Italy), *Environ. Int.*, 34, 665–670, 2008. 16380
- 30 Masiol, M., Rampazzo, G., Ceccato, D., Squizzato, S., and Pavoni, B.: Characterization of PM_{10} sources in a coastal area near Venice (Italy): an application of factor-cluster analysis, *Chemosphere*, 80, 771–778, 2010. 16381

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- Masiol, M., Squizzato, S., Ceccato, D., Rampazzo, G., and Pavoni, B.: A chemometric approach to determine local and regional sources of PM₁₀ and its geochemical composition in a coastal area, *Atmos. Environ.*, 54, 127–133, 2012a. 16380, 16381
- Nava, S., Becherini, F., Bernardi, A., Bonazza, A., Chiari, M., García-Orellana, I., Lucarelli, F., Ludwig, N., Migliori, A., Sabbioni, C., Udisti, R., Valli, G., and Vecchi, R.: An integrated approach to assess air pollution threats to cultural heritage in a semi-confined environment: the case study of Michelozzo's Courtyard in Florence (Italy), *Sci. Total Environ.*, 408, 1403–1413, 2010. 16378
- Pathak, R. K. and Chan, C. K.: Inter-particle and gas-particle interactions in sampling artifacts of PM_{2.5} in filter-based samplers, *Atmos. Environ.*, 39, 1597–1607, 2005. 16385
- Pathak, R. K., Louie, P. K. K., and Chan, C. K.: Characteristics of aerosol acidity in Hong Kong, *Atmos. Environ.*, 38, 2965–2974, 2004. 16383, 16386, 16388
- Pathak, R. K., Wu, W. S., and Wang, T.: Summertime PM_{2.5} ionic species in four major cities of China: nitrate formation in an ammonia-deficient atmosphere, *Atmos. Chem. Phys.*, 9, 1711–1722, doi:10.5194/acp-9-1711-2009, 2009. 16379, 16383, 16384, 16385, 16387, 16388, 16400
- Pathak, R. K., Wang, T., Ho, K. F., and Lee, S. C.: Characteristics of summertime PM_{2.5} organic and elemental carbon in four major Chinese cities: implications of high acidity for water-soluble organic carbon (WSOC), *Atmos. Environ.*, 45, 318–325, 2011. 16383
- Pope, C. A. III, Ezzati, M., and Dockery, D. W.: Fine-particulate air pollution and life expectancy in the United States, *N. Engl. J. Med.*, 360, 376–386, 2009. 16379
- Prodi, F., Belosi, F., Contini, D., Santachiara, G., Di Matteo, L., Gambaro, A., Donato, A., and Cesari, D.: Aerosol fine fraction in the Venice Lagoon: particle composition and sources, *Atmos. Res.*, 92, 141–150, 2009. 16380
- Putaud, J. P., Raes, F., Van Dingenen, R., Brüggemann, E., Facchini, M.-C., Decesari, S., Fuzzi, S., Gehrig, R., Hüglin, C., Laj, P., Lorbeer, G., Maenhaut, W., Mihalopoulos, N., Müller, K., Querol, X., Rogriguez, S., Schneider, J., Spindler, G., ten Brink, H., Tørseth, K., and Wiedensohler, A.: A European aerosol phenomenology – 2: chemical characteristics of particulate matter at kerbside, urban, rural and background sites in Europe. *Atmos. Environ.*, 38, 2579–2595, 2004. 16380
- Putaud, J.-P., Van Dingenen, R., Alastuey, A., Bauer, H., Birmili, W., Cyrus, J., Flentje, H., Fuzzi, S., Gehrig, R., Hansson, H. C., Harrison, R. M., Herrmann, H., Hitztenberger, R., Hüglin, C., Jones, A. M., Kasper-Giebl, A., Kiss, G., Kousa, A., Kuhlbusch, T. A. J.,

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- Löschau, G., Maenhaut, W., Molnar, A., Moreno, T., Pekkanen, J., Perrino, C., Pitz, M., Puxbaum, H., Querol, X., Rodriguez, S., Salma, I., Schwarz, J., Smolik, J., Schneider, J., Spindler, G., ten Brink, H., Tursic, J., Viana, M., Wiedensohler, A., and Raes, F.: A European aerosol phenomenology – 3: physical and chemical characteristics of particulate matter from 60 rural, urban, and kerbside sites across Europe, *Atmos. Environ.*, 44, 1308–1320, 2010. 16379
- Querol, X., Alastuey, A., Ruiz, C. R., Artiñano, B., Hansson, H. C., Harrison, R. M., Buringh, E., ten Brink, H. M., Lutz, M., Bruckmann, P., Straehl, P., and Schneider, J.: Speciation and origin of PM₁₀ and PM_{2.5} in selected European cities, *Atmos. Environ.*, 38, 6547–6555, 2004. 16380
- Rampazzo, G., Masiol, M., Visin, F., Rampado, E., and Pavoni, B.: Geochemical characterization of PM₁₀ emitted by glass factories in Murano, Venice (Italy), *Chemosphere*, 71, 2068–2075, 2008a. 16381
- Rampazzo, G., Masiol, M., Visin, F., and Pavoni, B.: Gaseous and PM₁₀-bound pollutants monitored in three environmental conditions in the Venice area (Italy), *Water Air Soil Pollut.*, 195, 161–176, 2008b. 16381
- Renner, E. and Wolke, R.: Modelling the formation and atmospheric transport of secondary inorganic aerosols with special attention to regions with high ammonia emissions, *Atmos. Environ.*, 44, 1904–1912, 2010. 16380
- Salvador, P., Artiñano, B., Alonso, D. G., Querol, X., and Alastuey, A.: Identification and characterisation of sources of PM₁₀ in Madrid (Spain) by statistical methods, *Atmos. Environ.*, 38, 435–447, 2004. 16388
- Schaap, M., van Loon, M., ten Brink, H. M., Dentener, F. J., and Buitjes, P. J. H.: Secondary inorganic aerosol simulations for Europe with special attention to nitrate, *Atmos. Chem. Phys.*, 4, 857–874, doi:10.5194/acp-4-857-2004, 2004a. 16380
- Schaap, M., Spindler, G., Schulz, M., Acker, K., Maenhaut, W., Berner, A., Wieprecht, W., Streit, N., Müller, K., Brüggemann, E., Chi, X., Putaud, J. P., Hitztenberger, R., Puxbaum, H., Baltensperger, U., and ten Brink, H.: Artefacts in the sampling of nitrate studied in the “INTERCOMP” campaigns of EUROTRAC-AEROSOL, *Atmos. Environ.*, 38, 6487–6496, 2004b. 16384
- Seinfeld, J. H. and Pandis, S. N.: *Atmospheric Chemistry and Physics – From Air Pollution to Climate Change*, 2nd edn., John Wiley & Sons, New York, USA, 2006. 16379, 16387

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- Squizzato, S., Masiol, M., Innocente, E., Pecorari, E., Rampazzo, G., and Pavoni, B.: A procedure to assess local and long-range transport contributions to PM_{2.5} and secondary inorganic aerosol, *J. Aerosol Sci.*, 46, 64–76, 2012. 16380, 16381, 16382, 16391
- Stockwell, W. R., Watson, J., Robinson, N. F., Steiner, W., and Sylte, W. W.: The ammonium nitrate particle equivalent of NO_x emissions for wintertime conditions in Central California's San Joaquin Valley, *Atmos. Environ.*, 34, 4711–4717, 2000. 16380, 16388
- Stockwell, W. R., Kuhns, H., Etyemezian, V., Green, M. C., Chow, J. C., and Watson, J. G.: The Treasure Valley secondary aerosol study II: modeling of the formation of inorganic secondary aerosols and precursors for Southwestern Idaho, *Atmos. Environ.*, 37, 525–534, 2003. 16379
- Vecchi, R., Valli, G., Fermo, P., D'Alessandro, A., Piazzalunga, A., and Bernardoni, V.: Organic and inorganic sampling artefacts assessment, *Atmos. Environ.*, 43, 1713–1720, 2009. 16384, 16385
- Wang, Y., Zhuang, G., Tang, A., Yuan, H., Sun, Y., Chen, S., and Zheng, A.: The ion chemistry and the source of PM_{2.5} aerosol in Beijing, *Atmos. Environ.*, 39, 3771–3784, 2005. 16390
- Zhang, Y., Seigneur, C., Seinfeld, J. H., Jacobson, M., Clegg, S. L., and Binkowski, F. S.: A comparative review of inorganic aerosol thermodynamic equilibrium modules: similarities, differences, and their likely causes, *Atmos. Environ.*, 34, 117–137, 2000. 16383
- Zhang, Q., Jemenez, J. L., Worsnop, D. R., and Canagaratna, M.: A case study of urban particle acidity and its influence on secondary organic aerosol, *Environ. Sci. Technol.*, 41, 3213–3219, 2007. 16383, 16384, 16386

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Table 1. Descriptive statistics (mean ± 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		IND 30	Summer		
		SRC 37	UBG 37		SRC 36	UBG 36	IND 31
	PM _{2.5}	26.8 ± 22.1	36.8 ± 31.3	32.0 ± 17.7	11.2 ± 4.7	14.5 ± 4.8	17.9 ± 14.2
	SO ₄ ²⁻	2.4 ± 1.3	2.4 ± 1.8	2.4 ± 1.0	2.7 ± 1.5	2.7 ± 1.6	3.4 ± 3.7
	ssSO ₄ ²⁻	0.05 ± 0.03	0.07 ± 0.07	0.13 ± 0.11	0.03 ± 0.02	0.07 ± 0.08	0.07 ± 0.05
	nssSO ₄ ²⁻	2.3 ± 1.3	2.3 ± 1.8	2.3 ± 1.0	2.7 ± 1.5	2.6 ± 1.6	3.7 ± 3.7
	NO ₃ ⁻	5.8 ± 6.4	6.4 ± 8.3	5.4 ± 4.2	0.9 ± 0.7	0.5 ± 0.5	0.7 ± 0.8
	NH ₄ ⁺	2.2 ± 2.0	2.4 ± 2.8	2.3 ± 1.3	1.1 ± 0.7	1.0 ± 0.6	0.9 ± 0.5
	SIA	10.2 ± 9.5	11.1 ± 12.6	10.0 ± 5.9	4.6 ± 2.3	4.1 ± 2.2	4.9 ± 4.5
	SIA/PM _{2.5}	36.3 ± 5.7	26.4 ± 8.6	31.7 ± 8.7	41.5 ± 10.7	26.4 ± 7.5	26.1 ± 6.1
	SO ₂	–	4.6 ± 3.2	6.6 ± 4.0	–	5.3 ± 3.8	5.0 ± 3.2
	NO	–	20.5 ± 20.6	27.5 ± 23.7	–	3.4 ± 3.4	7.4 ± 4.7
	NO ₂	–	48.1 ± 15.4	34.6 ± 11.5	–	36.1 ± 9.3	29.4 ± 6.3
	NO _x	–	73.1 ± 44.6	76.9 ± 46.8	–	32.0 ± 13.4	40.7 ± 12.2
	T	9.0 ± 2.2	10.5 ± 2.2	10.8 ± 2.2	22.6 ± 2.1	24.6 ± 2.2	24.2 ± 2.2
	RH	82.2 ± 13.7	78.7 ± 13.5	76.0 ± 13.4	79.0 ± 7.8	74.7 ± 6.0	74.9 ± 6.1
	NR	0.8 ± 0.2	0.8 ± 0.2	0.9 ± 0.2	0.8 ± 0.2	0.8 ± 0.1	0.7 ± 0.3
	SOR	–	0.28 ± 0.16	0.22 ± 0.09	–	0.28 ± 0.13	0.31 ± 0.20
	NOR	–	0.07 ± 0.07	0.10 ± 0.05	–	0.01 ± 0.01	0.02 ± 0.02
N		29	26	18	30	20	19
	[H ⁺] _{Total}	28.7 ± 26.9	22.1 ± 25.2	19.5 ± 21.0	9.4 ± 6.3	7.8 ± 6.0	12.1 ± 10.7
	[H ⁺] _{ins}	6.1 ± 12.2	2.9 ± 4.7	0.2 ± 0.1	1.2 ± 1.1	1.2 ± 1.0	2.0 ± 1.7
	pH	3.4 ± 0.7	3.6 ± 0.4	3.9 ± 0.1	2.5 ± 0.7	2.3 ± 0.5	2.0 ± 0.5

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Table 1. Continued.

N		SRC	Autumn	IND	SRC	Winter	IND
		40	UBG 38	42	41	UBG 38	41
PM _{2.5}	μgm ⁻³	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 ₄ ²⁻	μgm ⁻³	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 ₄ ²⁻	μgm ⁻³	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 ₄ ²⁻	μgm ⁻³	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 ₃ ⁻	μgm ⁻³	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 ₄ ⁺	μgm ⁻³	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 ⁻³	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 _{2.5}	%	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 ₂	μgm ⁻³	–	2.1 ± 2.3	5.6 ± 5.3	–	3.5 ± 2.1	5.5 ± 4.1
NO	μgm ⁻³	–	19.9 ± 21.4	28.0 ± 24.2	–	35.0 ± 23.1	46.1 ± 31.0
NO ₂	μgm ⁻³	–	41.6 ± 10.0	38.1 ± 8.5	–	47.6 ± 12.4	47.2 ± 10.8
NO _x	μgm ⁻³	–	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 ⁺] _{Total}	nmolm ⁻³	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 ⁺] _{Ins}	nmolm ⁻³	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 ⁺] _{Total}	nmolm ⁻³	9.4 ± 6.3	7.8 ± 6.0	12.1 ± 10.7	390 ± 545	220 ± 225	65 ± 44	70 ± 58
[H ⁺] _{Ins}	nmolm ⁻³	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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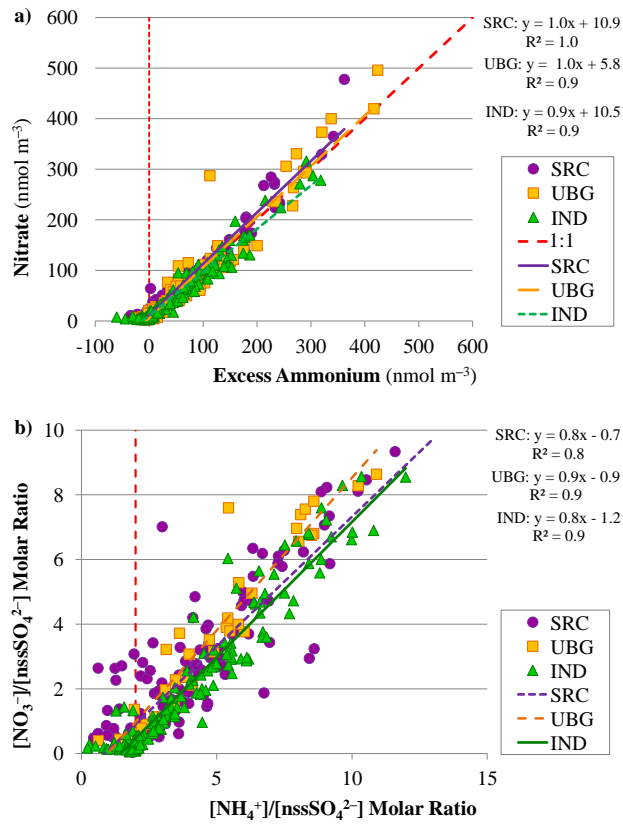


Fig. 3. Nitrate concentrations as a function of excess ammonium (a) and nitrate-to-sulfate molar ratio as a function of ammonium-to-sulfate molar ratio (b).

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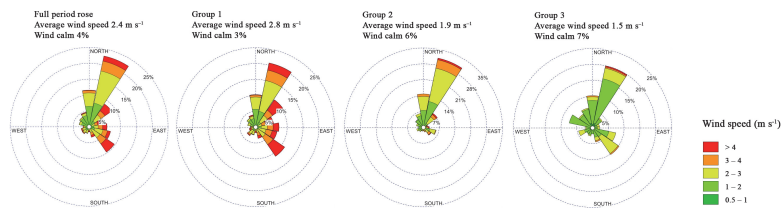


Fig. 4. Wind rose computed for each group identified by qHCA for UBG site.

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