Aerosol and Air Quality Research, 13: 1282–1296, 2013

ISSN: 1680-8584 print / 2071-1409 online
doi: 10.4209/aaqr.2012.11.0328

Insights into Chemical Coupling among Acidic Gases, Ammonia and Secondary Inorganic Aerosols

Sailesh N. Behera, Raghu Betha, Rajasekhar Balasubramanian*

Department of Civil and Environmental Engineering, National University of Singapore, 117576, Singapore

ABSTRACT

This study has investigated the chemical association among acidic gases, ammonia and secondary inorganic aerosols based on hourly measurements in a tropical urban atmosphere. The 24 hr average concentrations of SO_2, NH_3, HONO, HNO_3 and HCl were 21.77, 2.47, 1.73, 3.00 and 0.08 μg/m^3, respectively while those of SO_4^{2-}, NO_3^-, Cl^-, Na^+, K^+, NH_4^+, Ca^{2+} and Mg^{2+} in $PM_{2.5}$ were 4.41, 1.29, 0.28, 0.30, 0.32, 1.76, 0.14 and 0.07 μg/m^3, respectively. The results of this study for SO_2, NH_3, HONO, HCl, SO_4^{2-} and Cl^- showed significant diurnal variations, whereas there was a lack of significant diurnal variations for HNO_3, NO_3^-, Na^+, NH_4^+, Ca^{2+} and Mg^{2+}. Analysis of the charge balance of ionic species indicated that sufficient NH_3 was present most of the time to neutralize both H_2SO_4 and HNO_3 to form $(NH_4)_2SO_4$ and NH_4NO_3. The conversion of SO_2 into SO_4^{2-} and HNO_3 into NO_3^- was observed to be sensitive to changes in temperature and relative humidity, respectively. The study area experienced ambient relative humidity, which was higher than the estimated deliquescence relative humidity of NH_4NO_3 most of the time during the measurement period. As a result, the NH_4NO_3 formation was thermodynamically favorable during both daytime and nighttime. However, NH_4Cl formation was not favored under ammonia-poor conditions. It was observed that biomass burning could trigger nitrate and chloride formation in the ambient air.

Keywords: Secondary inorganic aerosol; Acid gases; Gas-to-particle conversion; Diurnal variation; Semi-volatile particulates; Ammonia.

INTRODUCTION

Fine particulate matter ($PM_{2.5}$) plays a significant role in atmospheric visibility reduction through the formation of haze, human health effects and climate change from the regional to global scale (Charlson and Heintzenberg, 1995; Vedal, 1997; IPCC, 2007). A significant portion of $PM_{2.5}$ is formed in the atmosphere through chemical transformations of precursor gases such as nitrogen oxides (NO_x), sulfur dioxide (SO_2), and ammonia (NH_3). This gas-to-particle conversion occurs either by condensation, which adds mass onto pre-existing aerosols, or by direct nucleation of these precursor gases (Baek and Aneja, 2004; Song *et al.*, 2006). The major inorganic compounds formed through the gas-to-particle formation process are ammonium bisulfate (NH_4HSO_4), ammonium sulfate $(NH_4)_2SO_4$, ammonium nitrate (NH_4NO_3) and ammonium chloride (NH_4Cl). NH_4HSO_4 and $(NH_4)_2SO_4$ are non-volatile in nature whereas NH_4NO_3 and NH_4Cl are semi-volatile. These secondary inorganic aerosols (SIA) are formed by reactions involving the only alkaline gas in the atmosphere, NH_3, with sulfuric acid (H_2SO_4), nitric acid (HNO_3) and hydrochloric acid (HCl) (Lin and Cheng, 2007; Aneja *et al.*, 2009; Behera and Sharma, 2011). SIA, represented by ionic species of SO_4^{2-}, NO_3^-, NH_4^+ and Cl^-, can account for 20–48% of the mass of $PM_{2.5}$ (Balasubramanian *et al.*, 2003; Lin and Cheng, 2007; Weijers *et al.*, 2011).

The secondary gaseous pollutants such as nitrous acid (HONO), HNO_3 and H_2SO_4 are produced from natural and manmade emissions of primary gas phase pollutants, NO_x and SO_2, through photochemical reactions (Derwent *et al.*, 2010). HCl, a precursor responsible for SIA formation, is mainly emitted by biomass burning, coal combustion and waste combustion (Bari *et al.*, 2003). The affinity of H_2SO_4 for NH_3 is much larger than that of HNO_3 and HCl for NH_3. As a result, the available ambient NH_3 is first taken up by H_2SO_4 to form $(NH_4)_2SO_4$ or NH_4HSO_4 (Ianniello *et al.*, 2011). The excess available NH_3 may react with HNO_3 and HCl to form NH_4NO_3 and NH_4Cl. Because of the semi-volatile nature of NH_4NO_3 and NH_4Cl and the existence of the thermodynamic equilibrium between precursor gases (HCl, HNO_3 and NH_3) and particulate ammonium salts, the formation mechanisms are rather complex (Trebs *et al.*, 2004; Finlayson-Pitts and Pitts, 2006).

* Corresponding author. Tel.: 65-65165135;
Fax: 65-68725483
E-mail address: ceerbala@nus.edu.sg

A number of studies (e.g., Nakajima *et al.*, 1999; Muraleedharan *et al.*, 2000) on atmospheric aerosol composition in tropical urban environments situated in Southeast Asia (SEA) have been reported, but most of these studies were focused on measuring specific aerosol components in biomass burning impacted air masses over a limited period of time. Some recent studies (e.g., Balasubramanian *et al.*, 2003; Abas *et al.*, 2004; Balasubramanian and Qian, 2004; See *et al.*, 2006; See *et al.*, 2007; Hyer and Chew, 2010) have investigated the status of air quality in SEA, notably Singapore and Malaysia, in detail. However, these studies did not fully address the chemical coupling among SIA and their corresponding precursor gases, which is important from both scientific and regulatory perspectives. In the past, several studies dealing with simultaneous measurements of SIA and the precursor gases have been reported from other regions of the World including Europe, U.S.A., China, and India (e.g., Bari *et al.*, 2003; Pavlovic *et al.*, 2006; Hu *et al.*, 2008; Wu *et al.*, 2009; Behera and Sharma, 2010; Ianniello *et al.*, 2011; Gómez-González *et al.*, 2012). However, the climatic conditions of SEA are quite different from those in other regions of the world, and characterized by high temperature and humidity throughout the year. Therefore, the chemistry behind the formation of SIA in tropical countries in SEA is expected to be different from what has been reported in other studies. To verify this hypothesis, systematic measurements of ionic species of $PM_{2.5}$ and the precursor gases on the time resolution of 1 hr are needed. Previous measurements of gaseous and particulate species on a daily (24 hr) basis, or 12 hr basis elsewhere (e.g., Bari *et al.*, 2003; Pavlovic *et al.*, 2006; Hu *et al.*, 2008; Wu *et al.*, 2009; Behera and Sharma, 2010; Ianniello *et al.*, 2011; Gómez-González *et al.*, 2012) could not explain the formation of SIA convincingly during different hours of the day. Moreover, there are concerns over the measurements of semi-volatile particulates due to artifact effects.

The novelty of the work addressed in the present study is that we provide deep insights into the formation of SIA based on hourly observations of acidic gases, ammonia and particulate-phase water soluble inorganic ions in a tropical environment in Southeast Asia for the first time. These hourly concurrent measurements eliminated the artifact effects associated with integrated measurements of semi-volatile particles. In this study, we used an online analyzer of model ADI 2080 (Monitoring of AeRosols and Gases, MARGA, Applikon Analytical B. V. Corp., Netherlands) with a $PM_{2.5}$ inlet to measure the mass concentrations of major water-soluble aerosol inorganic ions, ammonia and acidic gases at the time resolution of 1 hr from 14 September to 8 November, 2011. This time period represents the dry season in Southeast Asia during which time, biomass burning-impacted air masses are usually advected from Indonesia over the region, causing smoke haze episodes, under the influence of the Southwest monsoon (Balasubramanian *et al.*, 2003; See *et al.*, 2007). The specific objectives of the study were as follows: (1) simultaneous measurements of gaseous species (SO_2, NH_3, HONO, HNO_3 and HCl) and water soluble inorganic components of $PM_{2.5}$ (Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+, NO_3^-, SO_4^{2-} and Cl^-); (2) investigation of their temporal as well as diurnal trends during the measurement period; (3) examination of the relationship between meteorology and chemical equilibrium involved in the formation of semi-volatile aerosol components (NH_4NO_3 and NH_4Cl).

MATERIALS AND METHODS

The Study Area

The study area, Singapore (Fig. 1.), is located at the southern tip of the Malayan Peninsula, between latitudes 1°09'N and 1°29'N and longitudes 103°36'E and 104°25'E, and measures 42 km from east to west and 23 km from north to south (Balasubramanian *et al.*, 2003). The measurement of air quality and meteorology parameters was conducted on an hourly basis for two months at the Atmospheric Research Station (67 m above the sea level and about 1 km from the open sea), National University of Singapore. The details of the characteristics of the sampling site and study area are described in Balasubramanian *et al.* (2003). This is to be noted that the study area reported in the earlier study of Balasubramanian *et al.* (2003) is the same as the one used in the present study.

According to the National Environmental Agency (NEA), the main sources of air pollution in Singapore are from the burning of fossil fuel for heat generation in industries, electricity generation and transportation (http://app2.nea.gov.sg/psi_faqairquality.aspx). The other important source is trans-boundary air pollution, which includes the transport of air pollutants from biomass fires in the region (e.g., Indonesia, Malaysia and Brunei). The past biomass burning (smoke haze) episodes occurred largely within the period of May to October due to uncontrolled forest fires in the region, and the prevailing Southwest Monsoon winds blew the smoke from fires in Indonesia to Singapore (Balasubramanian *et al.*, 2003; See *et al.*, 2006).

The NEA has been implementing all possible control options to reduce emissions of air pollutants from vehicular and industrial sources in order to improve the air quality status in Singapore. However, the pollution status in Singapore is still under scrutiny because of the concerns over the ambient $PM_{2.5}$ levels not meeting the goals of World Health Organization. For example, Fig. 2 shows the trends of annual averages of ambient level of $PM_{2.5}$ concentration from year 2005 through 2011.

Sampling and Chemical Analysis

The duration of measurements of both ambient aerosol and gaseous species was from 0:00 to 23:00 for each day on a time resolution of 1 hr from 14 September through 8 November, 2011. For the purpose of data interpretation, we classified the time as 7:00 to 19:00 for daytime and 19:00 to 7:00 for nighttime based on the timings of sunrise and sunset during this period (http://www.timeanddate.com/). A model ADI 2080 online analyzer (MARGA, Applikon Analytical B. V. Corp., Netherlands) with a $PM_{2.5}$ inlet was used to measure the mass concentrations of gases and particulate species at the time resolution of 1 hr. The MARGA system was set to draw ambient air into the

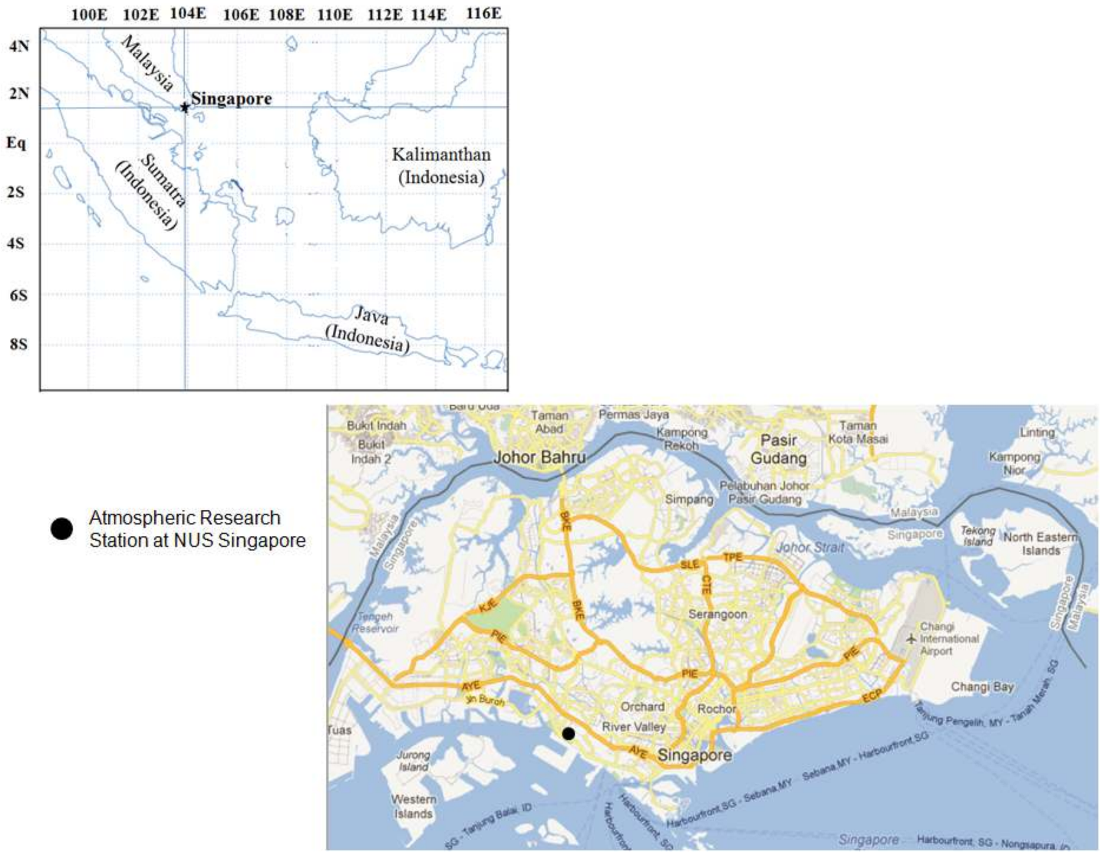

Fig.1. Map showing study area Singapore and its neighboring regions in the Southeast Asia and location of Atmospheric Research Centre at NUS, Singapore. The maps are retrieved from HYPSLIT model and Google map.

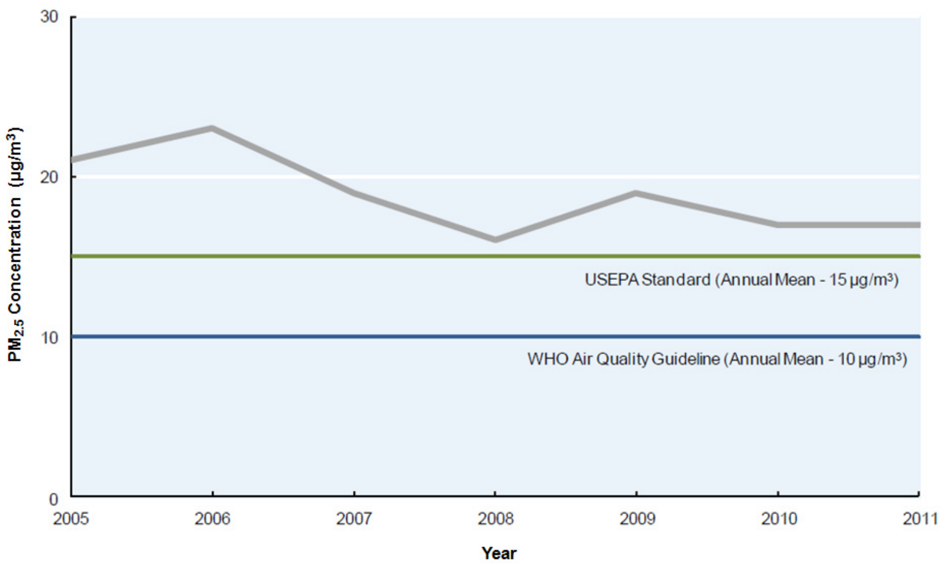

Fig. 2. Trends of annual average of ambient concentration of $PM_{2.5}$ in Singapore. (Adapted from EPD Annual Report, 2011).

sampling box at a flow rate of 1 m^3/h through an inlet, and exhibited a particle collection efficiency of 99.7%. The gaseous species were captured in the liquid film (0.0035% H_2O_2) formed by one Wet Rotating Denuder (WRD). Fine particles in the residual airflow went through the supersaturated steam (0.0035% H_2O_2, 120–140°C) erupted out from one Steam Jet Aerosol collector (SJAC), and were pooled into its collector. MARGA utilized a WRD to collect acidic gases and NH_3 by diffusion into an aqueous film. The aqueous solutions from the WRD and SJAC were subsequently analyzed by an online ion chromatograph (IC) for water-soluble anions and cations.

MARGA has the capability of measuring the hourly average concentrations of NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, NO_3^-, Cl^-, HCl, HONO, SO_2, HNO_3, NH_3 in the atmosphere with the detection limits for all the components were 0.1 μg/m^3 or better, except for K^+ (0.16 μg/m^3), Mg^{2+} (0.12 μg/m^3) and Ca^{2+} (0.21 μg/m^3) as reported by Makkonen *et al.* (2012). During the measurement period, MARGA was calibrated using the internal standard solution (LiBr) every week to verify accurate detecting limits and to ensure data quality. Field blanks were used and suitable corrections made as recommended by Makkonen *et al.* (2012). A total of 1038 number valid hourly observations were made for each chemical species over a period of 45 days for further interpretation. During the measurement period, meteorological parameters (temperature, relative humidity and rainfall) were recorded using the Solus™ meteorological system (Texas Electronics) installed on the roof of the research station with a time resolution of 1 hr. A Data acquisition system for measuring concentrations of gases, aerosols and meteorology was housed in a thermally controlled laboratory room.

Non-Sea-Salt Components in $PM_{2.5}$

As the sampling site is located near to the sea surface (about 1000 m away from sea), we attempted to estimate aerosol components which are free from the sea salt influence. The concentrations of non-sea-salt sulfate (nss-SO_4^{2-}), non-sea-salt K^+ (nss-K^+) and non-sea-salt Ca^{2+} (nss-Ca^{2+}) were estimated by the following equations and by assuming that the chemical composition of sea-salt particles is the same as that of seawater, and that the soluble Na^+ in particulate samples comes solely from sea salts (Kennish, 1994; Balasubramanian *et al.*, 2003):

$$\text{nss-}SO_4^{2-} = [SO_4^{2-}] - 0.2516 \times [Na^+] \quad (1)$$

$$\text{nss-}K^+ = [K^+] - 0.037 \times [Na^+] \quad (2)$$

$$\text{nss-}Ca^{2+} = [Ca^{2+}] - 0.0385 \times [Na^+] \quad (3)$$

RESULTS AND DISCUSSIONS

Overall Results

Table 1 provides a statistical summary of the measured 24 hr mean concentrations of gaseous pollutants and particulate inorganic ions in $PM_{2.5}$. It should be noted that in this paper, all reported (as presented in Table 1) and interpreted values (in the section on 'Results and Discussions') for the levels of SO_4^{2-}, K^+ and Ca^{2+} represent non-sea-salt components. Overall, 24 hr mean concentrations of total (non-sea-salt and sea-salt) SO_4^{2-}, K^+ and Ca^{2+} were observed as 4.48 ± 1.76 μg/m^3, 0.31 ± 0.14 μg/m^3, and 0.14 ± 0.04 μg/m^3, respectively. The measured mean concentrations of acid gases, inorganic ions and meteorological parameters (temperature and relative humidity) are compared to those from other urban areas of the world in Tables 2 and 3. The overall meteorology of Singapore is characterized by higher humidity than that in other cities of the world (Tables 2 and 3). The role of the prevailing humid conditions in the chemistry of SIA formation is examined in a subsequent section. The overall level of SO_2 in Singapore is not significantly different from what was reported from other cities of the World. The NH_3 concentration is comparable to that from Nara, Japan (Matsumato and Okita, 1998), but is otherwise lower than those from other areas of the World. The ambient concentrations of HONO and HNO_3 are comparable to those from New York and Taiwan (Bari *et al.*, 2003; Lin *et al.*, 2006) while the level of HCl in Singapore is less than those from other areas of the world (Table 2).

Similar comparisons are made for major $PM_{2.5}$ chemical components in Singapore with those from other cities of the world (Table 3). In general, the measured mean concentrations from this study are comparable to those from New York and Milan (Qin *et al.*, 2006; Lonati *et al.*, 2008). From Table 2, it has been observed that two conditions of ammonia availability prevail in the ambient air: (i) ammonia-poor conditions (molar ratio of (NH_4^+/SO_4^{2-}) < 2.0) and (iii) ammonia-rich conditions (molar ratio of (NH_4^+/SO_4^{2-}) ≥ 2.0). This study had experienced a molar ratio of NH_4^+/SO_4^{2-} as 2.2, which indicated the atmosphere

Table 1. Statistical summary of air quality on a 24 hr basis (unit: μg/m^3).

Species	N	Mean	S.D.	Min	Max	Median
SO_2	45	21.77	15.41	2.39	78.62	18.18
NH_3	45	2.47	2.32	0.53	12.71	1.77
HONO	45	1.73	0.89	0.46	4.91	1.69
HNO_3	45	3.00	1.52	0.67	6.80	3.03
HCl	44	0.08	0.08	0.03	0.57	0.06
SO_4^{2-}*	45	4.41	1.76	1.25	8.00	4.63
NO_3^-	45	1.29	0.30	0.88	2.03	1.25
Cl^-	45	0.28	0.19	0.07	1.02	0.24
Na^+	45	0.30	0.10	0.17	0.61	0.28
K^+*	45	0.32	0.14	0.16	0.71	0.30
NH_4^+	45	1.76	0.71	0.52	3.77	1.53
Ca^{2+}*	45	0.14	0.05	0.02	0.26	0.14
Mg^{2+}	45	0.07	0.02	0.04	0.13	0.06

* the concentrations reported are for non sea salt particles; N for number of valid observations; S.D. for standard deviation; Min for minimum; Max for maximum.

Table 2. Comparison of levels of gaseous species and meteorology with other studies in the world (μg/m^3).

Location	Gaseous species (μg/m^3)					Meteorology		Remarks	Reference
	SO_2	NH_3	HONO	HNO_3	HCl	Temp (°)	RH (%)		
Nara, Japan	4.3	2.4	1.5	1.6	1.7	19.0	NA	Annual average	Matsumato and Okita, 1998
New York, USA	18.7	4.3	2.0	3.6	0.9	NA	NA	Summer season at Manhattan site	Bari *et al.*, 2003
Seoul, South Korea	6.6	5.2	7.8	0.6	NA	12.5	58.3	Fall season	Kang *et al.*, 2004
Taichung, Taiwan	NA	8.5	1.9	2.6	NA	24.2	68.7	Annual average	Lin *et al.*, 2006
Lahore, Pakistan	19.4	50.1	19.6	1.0	1.2	15.0	65.0	Winter season	Biswas *et al.*, 2008
Pearl River Delta, China	55.4	7.3	2.9	6.3	2.8	26.2	63.7	Autumn season	Hu *et al.*, 2008
Beijing, China	14.1	16.6	3.6	1.9	0.6	NA	NA	Summer season	Wu *et al.*, 2009
Kanpur, India	21.7	22.3	NA	7.2	NA	24.5	58.5	Average of summer and winter seasons	Behera and Sharma, 2010
Singapore	21.8	2.5	1.7	3.0	0.1	26.2	76.3	Dry season with Southwest monsoon (no specific season)	This study

NA represents "not available".

Table 3. Comparison of levels of $PM_{2.5}$ characteristics with other studies in the world.

Location	Levels of major ions (μg/m^3)					Molar ratios of SIA components			Meteorology		Remarks	Reference
	K^+	NH_4^+	Cl^-	NO_3^-	SO_4^{2-}	NH_4^+/SO_4^{2-}	NH_4^+/NO_3^-	$NH_4^+/(2 \times SO_4^{2-} + NO_3^- + Cl^-)$	Temp (°)	RH (%)		
Pearl River Delta, China	NA	9.2	2.4	7.2	24.1	2.0	4.4	0.7	26.2	63.7	Autumn season	Hu *et al.*, 2008
Guangzhou, China	1.4	7.3	2.4	9.5	21.6	1.8	2.6	0.6	21.3	72.6	Spring season	Tao *et al.*, 2009
Seoul, South Korea	0.4	5.3	0.2	7.1	8.1	3.5	2.6	1.0	NA	NA	Annual average	Heo *et al.*, 2009
Beijing, China	NA	12.5	NA	14.2	20.8	3.2	3.0	1.0	NA	NA	Dry season	Kim Oanh *et al.*, 2006
Bangkok, Thailand	NA	1.6	NA	1.2	5.6	1.5	4.6	0.7	NA	NA	Dry season	Kim Oanh *et al.*, 2006
Milan, Italy	NA	3.0	0.3	8.7	4.7	3.4	1.2	0.7	NA	NA	Average of warm and cold seasons	Lonati *et al.*, 2008
NewYork, USA	0.1	1.9	0.1	2.0	4.3	2.4	3.3	0.8	NA	NA	Annual average	Qin *et al.*, 2006
Lahore, Pakistan	3.5	16.1	7.4	18.9	19.2	4.5	2.9	1.0	15.0	65.0	Winter season	Biswas *et al.*, 2008
Kanpur, India	2.6	15.7	2.3	19.8	27.6	3.0	2.7	0.9	24.5	58.5	Average of summer and winter seasons	Behera and Sharma, 2010
Lanzhou, China	0.8	4.1	5.5	3.2	9.8	2.2	4.4	0.6	25.0	45.0	Dry season	Pathak *et al.*, 2009
Durg, India	0.9	2.1	2.1	3.2	6.8	1.6	2.3	0.5	26.4	64.0	Annual average	Deshmukh *et al.*, 2011
Nanchang, China	1.2	4.9	1.6	2.8	28.9	0.9	6.0	0.4	NA	NA	NA	Huang *et al.*, 2012
Gosan, Korea	0.3	3.3	0.2	1.2	9.6	1.8	9.5	0.8	NA	NA	Spring season	Stone *et al.*, 2011
Athens, Greece	0.1	0.9		0.5	4.0	1.2	6.2	0.5	NA	NA	Annual average	Remoundaki *et al.*, 2013
Singapore	0.3	1.8	0.3	1.3	4.4	2.2	4.6	0.8	26.2	76.3	Dry season with Southwest monsoon (no specific season)	This study

NA represents "not available".

as ammonia-rich condition. However, the ammonium equivalent concentration is less than the sum of sulfate, nitrate and chloride (Table 3). This might be the reason for lower levels of nitrates in the study area. The existing levels of nitrates may be due to nighttime enhancement of nitrates through heterogeneous hydrolysis of N_2O_5 and HNO_3 as has been explained in a recent study by Pathak *et al.* (2011).

To understand the role of precursor gases (SO_2, NH_3 and HCl) in the formation of secondary gaseous species (HONO and HNO_3) and SIA in $PM_{2.5}$ (NH_4^+, NO_3^-, SO_4^{2-} and Cl^-), correlation coefficients were estimated between various species using Minitab 15 English (as presented in Table S1). The major observation from this analysis revealed that NH_3 showed significant correlations with SO_4^{2-}, NO_3^-, and NH_4^+ (r = 0.36, 0.41, and 0.55 respectively with P < 0.01, 0.01, and 0.001) indicating that formation of secondary inorganic components of $PM_{2.5}$ is dependent on levels of NH_3. Significant correlations between SO_2-SO_4^{2-}, HNO_3-NO_3^-, NH_3-NH_4^+, NH_4^+-SO_4^{2-}, NH_4^+-NO_3^- were observed, suggesting chemical coupling between acidic gases, ammonia and the particulates to form $(NH_4)_2SO_4$ and NH_4NO_3 under ammonia-rich conditions.

Diurnal Variation of Pollutants

The hourly concentration data of gaseous and particulate species were classified into their daytime and nighttime values on the basis of the timing of sunrise and sunset. To assess the overall difference between daytime and nighttime levels of pollutants, a paired t-test with unequal variance was performed for each gaseous and particulate component using Minitab 15 English. From the results of the t-test, it was observed that SO_2, NH_3, HONO, HCl, SO_4^{2-} and Cl^- showed significant diurnal variations at 95% confidence level (P < 0.05). However, HNO_3, NO_3^-, Na^+, NH_4^+, Ca^{2+} and Mg^{2+} did not show any significant diurnal variations. The overall mean meteorological parameters observed during the measurement period were: (i) temperature: 26.8 ± 1.3°C (daytime) and 25.6 ± 0.9°C (nighttime); (ii) relative humidity: 72.9 ± 5.3% (daytime) and 79.7 ± 3.7% (nighttime), (iii) rainfall: 0.6 ± 0.9 mm (daytime) and 0.5 ± 1.2 mm (nighttime), and (iv) wind direction: 179.6 ± 57.6° (daytime) and 141.7 ± 62.4° (nighttime). These meteorological parameters were evaluated with paired t-test similar to air pollutant species to assess the diurnal variations. It was observed that temperature, relative humidity and rainfall showed significant diurnal variation at 95% confidence level (P < 0.05). The diurnal variations of the average temperature and relative humidity during the measuring period are shown in Fig. S1. Overall, the meteorological conditions in the study area were characterized by high humid conditions in the region.

A significant diurnal variation of NH_3 was observed with 'daytime/nighttime' = 1.8 and P = 0.01. The reason could be due to large evaporative emissions from several sources during the day time (e.g., NH_3 from grass leaves). The maximum NH_3 of 4.9 µg/m^3 was observed during 10:00 to 11:00 hr, and the minimum of 0.9 µg/m^3 was observed from 22:00 to 23:00 hr (Fig. 3(a1)). The maximum observed NH_3 levels could possibly be due to more evaporation of NH_3 from wet surfaces, such as grass leaves and sewerage systems due to more temperature and with moderate mixing layer during these hours of the day. From Fig. 3(a2), it can be clearly observed that NH_4^+ did not show any distinct peaks except two smaller peaks at 11:00 and 15:00 hr. These smaller peaks of NH_4^+ could be attributed to formation of NH_4NO_3 and $(NH_4)_2SO_4$ during more traffic emissions for NO_2 and more industrial emissions for SO_2.

Figs. 3(b1)–(b2) show the diurnal variations of SO_2 and SO_4^{2-} concentrations. Both SO_2 and SO_4^{2-} concentrations were observed to be higher during daytime with 'daytime/nighttime' = 2.2, (P < 0.0001) and 'daytime/nighttime' = 1.3 (P = 0.006), respectively. The higher levels of SO_4^{2-} during daytime could be explained through enhanced conversion of NH_3 and H_2SO_4 into $(NH_4)_2SO_4$ in the presence of higher solar radiation due to the presence of more OH radicals. The maxima of hourly concentrations of SO_2 occurred from 13:00 to 17:00 hr (maximum of 42.8 µg/m^3 at 15:00 hr). The reason for such high levels of SO_2 can be explained through the meteorology and industrial emissions. During these peak hours of SO_2, the observed wind direction was the SW direction, and this may be reason for transport of SO_2 from power plants and petroleum refineries located in the southwest direction of the measurement site. The concentration of SO_4^{2-} increased slightly from the early morning (5:00 to 6:00) and then decreased during 7:00–9:00 and increased from 9:00 and peaked during 14:00–15:00 hr. The reason for lower concentration during 7:00–8:00 due to cloud covers in the sky, which could obstruct the sunlight and thus provide unfavorable conditions for the production of OH radicals. It was also observed that during this hour, an average of 1.9 mm of rainfall was recorded at the measurement site.

From the hourly observations of HNO_3, it is clear that the maxima of HNO_3 concentration occurred as 3.4 µg/m^3 in the late afternoon (16:00–17:00) at a high temperature and low relative humidity (Fig. 3(c1)). The reason could be due to more solar radiation and dry conditions that favor formation of HNO_3 through the reaction of NO_2 and OH radical (Hoek *et al.*, 1996; Wu *et al.*, 2009).

The formation of NH_4NO_3 in the ambient air is expected to be more favorable during nighttime than daytime due to higher humid conditions in the night (Acker *et al.*, 2004; Behera and Sharma, 2012). However, in this study, we observed different trends on diurnal variations of NO_3^- concentrations with 'daytime/nighttime' = 0.96 that is not statistically significant (P = 0.57). To examine such diurnal trends of NO_3^-, we attempted to understand the mechanism behind the formation of NH_4NO_3, which is explained in a subsequent section of this paper. The levels of NO_3^- peaked at 8:00 (Fig. 3(c2)), when the relative humidity was observed to be high (83%).

Figs. 3(d1)–(d2) shows the diurnal variations of HCl and Cl^- concentrations. HCl was observed to be higher during daytime than nighttime with the 'daytime/nighttime' ratio being 1.5 (P = 0.04). However, Cl^- showed higher concentration during nighttime than daytime with 'daytime/nighttime' = 0.62 (P = 0.006). HCl is produced from the evaporation of NH_4Cl at high ambient temperatures. The levels of HCl peaked during 17:00–18:00 under dry

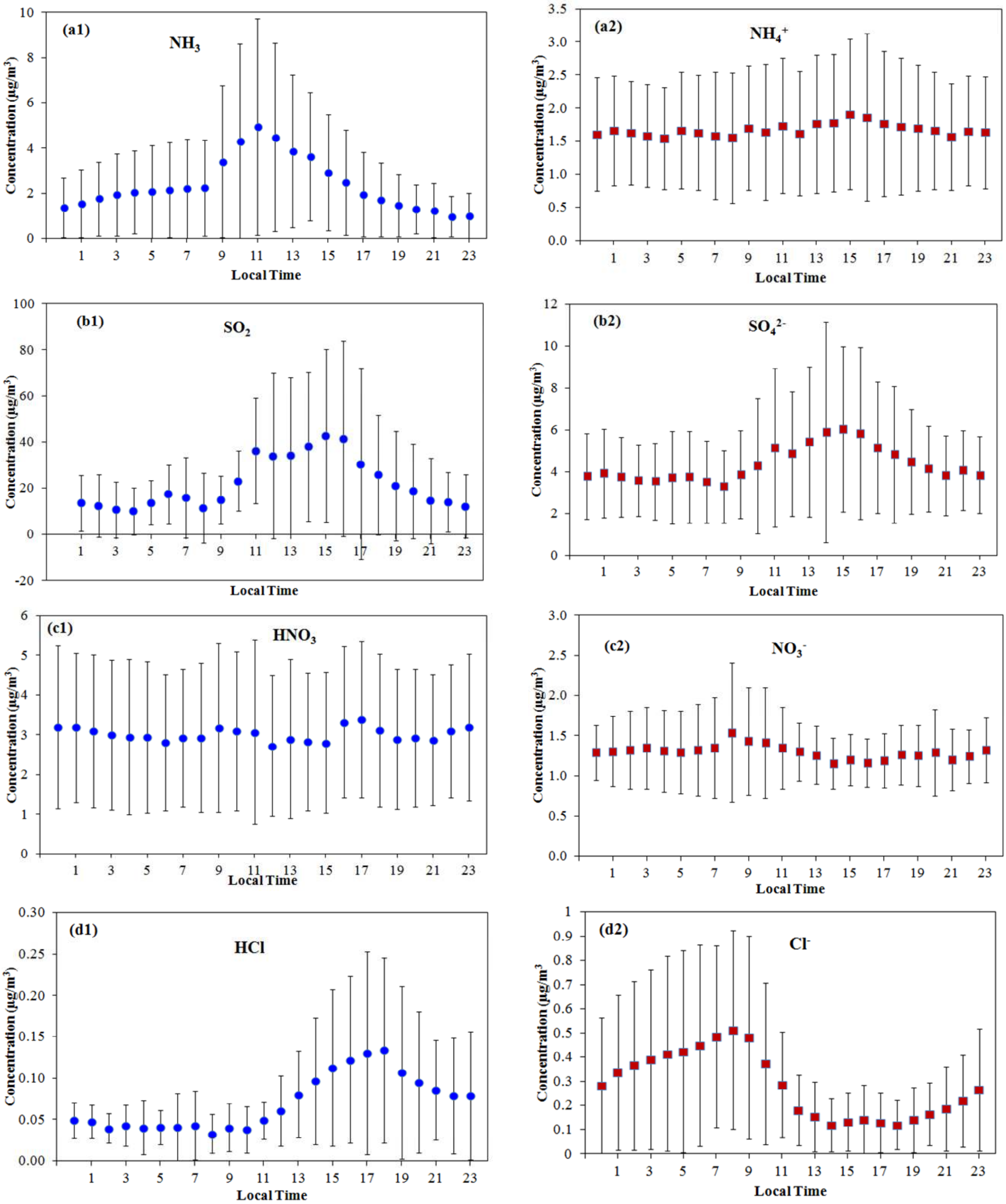

Fig. 3. Diurnal variations of NH_3, SO_2, HNO_3, and HCl and major ionic constituents in $PM_{2.5}$. The error bars represent the corresponding standard deviations.

conditions, whereas Cl^- peaked during 7:00–8:00 during more humid conditions. Our observations are similar to those in the study carried out by Hu *et al.* (2008). It should be noted that Cl^- did not show significant correlation with HCl ($r = 0.16$; Table S1) and showed a significant correlation with Na^+ ($r = 0.33$; Table S1; $P < 0.05$). Hence, the multiple sources of Cl^- could be confirmed with major contributions from sea-salt (NaCl), NH_3 (through neutralization of HCl to form NH_4Cl), or combustion activities, so it is difficult to draw any conclusion to explain for the reason of diurnal variations of Cl^-.

HONO was observed to be formed in the atmosphere during the nighttime hours as it tends to be photolyzed during the daytime, producing OH radicals during early hours of the day (Calvert *et al.*, 1994). Fig. 4 shows the diurnal variation of HONO with higher concentrations at nighttime and lower concentrations during daytime. This significant higher levels of HONO during nighttime with 'daytime/nighttime' = 0.72 (P = 0.006) can be explained by its heterogeneous formation and nighttime accumulation, i.e., reaction of N_2O_3 with moist aerosols (or other surfaces) to form two HONO molecules (Calvert *et al.*, 1994). Moreover, HONO can be formed by a heterogeneous reaction of NO_2 with H_2O, which can take place on wet surfaces, such as ground and aerosol particles (Stutz *et al.*, 2002; Wu *et al.*, 2009). In this study, the concentration of HONO increased from the early morning (6:00 hr) and peaked at 9:00 (2.7 µg/m^3) and then decreased till 17:00. It was observed by earlier studies (Hu *et al.*, 2008; Wu *et al.*, 2009) that the peak of HONO levels occurs during the sunrise. The possible reason for such maximum levels during sunrise could be due to decreasing humidity, leading to the evaporation of dew droplets containing dissolved HONO. Zhou *et al.* (2002) and Acker *et al.* (2004) also suggested that the release of the night-time trapped nitrous acid from the surfaces acted as a strong HONO source in the morning hours due to evaporation in dew droplets. This study finds slight deviations from earlier studies, which observed the highest levels of HONO at 9:00 and the sunrise took place at 7:00 during the measuring period. The cloud covers in the sky during 7:00–8:00 could have obstructed the morning sunlight, which is responsible for evaporation of more water vapors. The lower levels of HONO from 10:00 to 17:00 could be attributed to formation of OH radicals under high influx of solar radiation.

Charge Balance of Ionic Constituents of $PM_{2.5}$

Ions contributed a mean mass concentration of 9.1 µg/m^3 and 7.9 µg/m^3 to $PM_{2.5}$ during daytime and nighttime, respectively. On the basis of hourly data, the mean molar ratio of NH_4^+ to SO_4^{2-} was 2.2 ± 0.7 (n = 1038), mostly > 2, indicating the complete neutralization of H_2SO_4 with NH_3 to form $(NH_4)_2SO_4$. The excess of NH_4^+ was inferred to be associated with NO_3^- and Cl^-. Fig. 5(a) shows the charge balance between NH_4^+ and Cl^-, NO_3^-, and SO_4^{2-} (R^2 = 0.82 and P < 0.001 for n = 1038). The charge balance between all cations, and all inorganic anions was shown in Fig. 5(b) (R^2 = 0.80 and P < 0.001 for n = 1038). The charge balance (Fig. 5(b)) is well below 1:1 relationship indicating an excess of cations compared to anions. The possible explanation for deficiency of cations could be due to the fact that HCO_3^- and water-soluble organic anions (such as organic acidic ions) were not measured in this study. See *et al.* (2006, 2007) had reported that some of organic acids (e.g., acetate and formate) contribute significantly to the mass of $PM_{2.5}$ in Singapore. The charge balance in Fig. 5(a) was above and parallel to 1:1 line than the one in Fig. 5(b), confirming that substantial NH_4^+ was present to neutralize the acidic components (H_2SO_4, HNO_3 and HCl) to form $(NH_4)_2SO_4$, NH_4NO_3 and NH_4Cl.

'Excess ammonia' is an indicator of $PM_{2.5}$-NO_3^- formation, and signifies whether the atmospheric condition is limited by the availability of HNO_3 or NH_3 (Baker and Scheff, 2007); it can be expressed as Eq (4):

$$\text{Excess ammonia} = [NH_3] + [NH_4^+] - 2 \times [SO_4^{2-}] - [NO_3^-] - [HNO_3] \quad (4)$$

All the terms in Eq (4) are expressed in units of µmole/m^3. When the 'excess ammonia' term is < 0, then $PM_{2.5}$-NO_3^- formation would be NH_3-limited and when the term is > 0, then $PM_{2.5}$-NO_3^- formation is HNO_3-limited. In this study, mixed responses were observed for the 'excess ammonia' estimated values on the basis of hourly observations. Out of 1038 hourly data set, it was observed that 398 data sets were NH_3-limited conditions ('excess ammonia' = –0.039 ± 0.037 µmol/m^3) and 640 data sets were HNO_3-limited (excess ammonia = 0.144 ± 0.192 µmol/m^3). Overall, the study area experienced an 'excess ammonia' = 0.074 ± 0.176 µmol/m^3 with n = 1038. Under NH_3-limited conditions, the NO_3^- formation could occur from the hydrolysis of N_2O_5 under high humidity condition and/or heterogeneous reaction of HNO_3 on sea salt or soil dust particles (Yoshizumi and

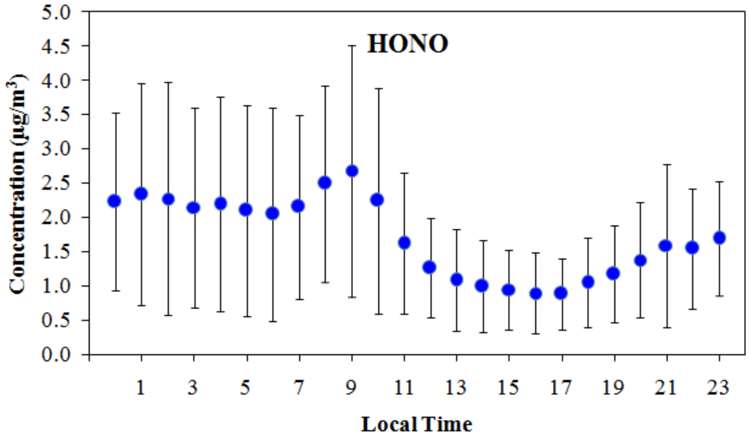

Fig. 4. Diurnal variations of HONO with the error bars representing standard deviations.

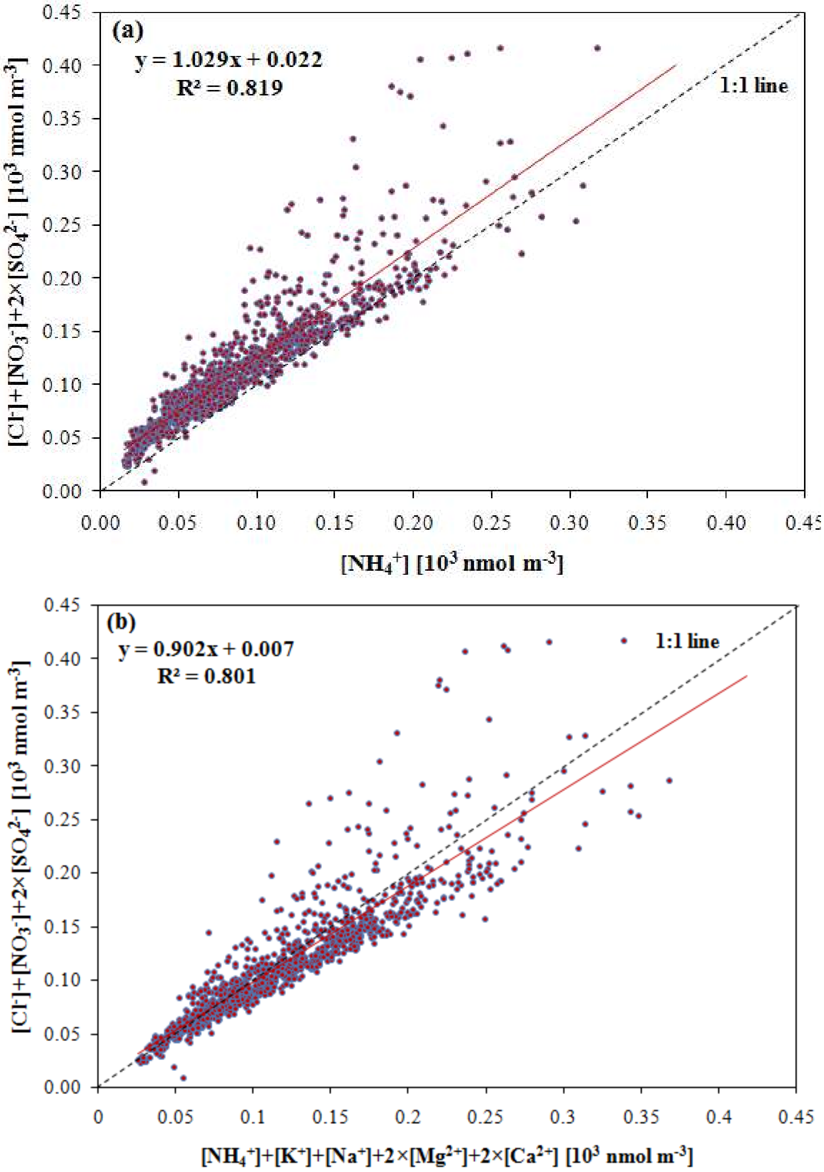

Fig. 5. Charge balance: (a) between Cl^-, NO_3^-, SO_4^{2-} and NH_4^+; (b) between Cl^-, NO_3^-, SO_4^{2-} and NH_4^+, K^+, Na^+, Ca^{2+}, and Mg^{2+}.

Hoshi, 1985; Pathak *et al.*, 2011). The NO_3^- production rate from heterogeneous hydrolysis of N_2O_5 may contribute to the enhancement of NO_3^- level during nighttime due to the highest production rate of N_2O_5 compared to daytime. It could be concluded that most of the times the atmosphere had sufficient NH_3 to neutralize both H_2SO_4 and HNO_3 to form $(NH_4)_2SO_4$ and NH_4NO_3.

Gas-to-Particle Formation

As discussed previously (Section 3.2), the levels of secondary species (HONO, HNO_3, NH_4^+, SO_4^{2-}, NO_3^- and Cl^-) showed different hourly patterns during the measurement period. To understand the role of meteorology (temperature and relative humidity) in the formation of these secondary species, correlation coefficients were estimated between these secondary species and meteorology using Minitab 15 English on a basis of 1 hr data (as presented in Table S2). Based on the correlations between temperature, relative humidity and other species, the following observations and conclusions can be made: (i) HONO showed positive correlation with NO_3^-, Cl^- and relative humidity, and negative correlation with SO_4^{2-} and temperature, indicating that more humid conditions favor the formation of HONO through the heterogeneous process from H_2O and NO_2; (ii) NH_4^+ showed significant correlations with SO_4^{2-} and NO_3^-, confirming that sufficient NH_3 was present to neutralize H_2SO_4 and HNO_3 during the measurement period. The higher correlation of NH_4^+ with SO_4^{2-} ($r = 0.89$) than with NO_3^- ($r = 0.46$) suggests that $(NH_4)_2SO_4$ is more likely to be formed than NH_4NO_3 because of better affinity between the two ions; (iii) an insignificant correlation of NH_4^+ with Cl^- ($r = 0.08$) indicates that in the study area NH_3 was not sufficiently large to allow its reaction with HCl and particulate Cl^- may also arise from other sources apart from

NH_4Cl; (iv) a positive correlation of NH_4^+ with temperature showed that daytime hours are favorable for conversion of NH_3 to its particulate ammonium salts; and (v) temperature showed significant correlation with SO_4^{2-} indicating the formation of particulate SO_4^{2-} is favored under higher OH radicals due to more solar radiation during daytime; (vi) negative correlations of NO_3^- and Cl^- with temperature justifies that the semi-volatile NH_4NO_3 and NH_4Cl species are subjected to reverse reactions with conversion back into gaseous NH_3 and HNO_3 and NH_3 and HCl, respectively; and (vii) positive correlations of NO_3^- and Cl^- with relative humidity confirmed that more humid conditions favor formations of NH_4NO_3 and NH_4Cl.

The partitioning of gas-to-particle phase of NH_4NO_3 and NH_4Cl strongly depends on the gas phase precursor concentrations, temperature, relative humidity (RH) and aerosol chemical composition (Pio and Harrison, 1987a, b; Mozurkewich, 1993; Seinfeld and Pandis, 2006). In Table S2, the relationship between NO_3^- and Cl^- concentrations, temperature and RH can clearly be observed. NO_3^- and Cl^- concentrations are basically anti-correlated with temperature and correlated with relative humidity. The observations are similar to the studies done by Rupakheti *et al.* (2005) and Hu *et al.* (2008) who related NO_3^- and Cl^- diurnal profiles to temperature and RH variations.

The transition from solid phase equilibrium to aqueous phase occurs, when RH increases, depending on ambient RH values compared to the Deliquescence Relative Humidity (DRH) of the particle. In contrast, the transition from aqueous phase to solid phase depends on ambient RH compared to the Efflorescence Relative Humidity (ERH), when ambient RH decreases. For example, at 298 K $(NH_4)_2SO_4$ particles have a DRH of 80% and an ERH of 35%, while NH_4NO_3 particles have a DRH of 62% and no ERH is observed (Martin *et al.*, 2003; Seinfeld and Pandis, 2006; Poulain *et al.*, 2011). Particles are observed to be in meta-stable state, when ambient RH values vary between DRH and ERH. Under such circumstances, the phase of the particles not only depends on the chemical composition of the particles, but also on the RH history of the particles (Martin *et al.*, 2003). In this study, we estimated the DRH of NH_4NO_3 and NH_4Cl on an hourly basis by using the empirical relations between temperature and DRH from Stelson and Seinfeld (1982a) and Pio and Harrison (1987a). Out of 1038 valid 1 hr data, it was found that: (i) NH_4NO_3: RH < DRH for n = 42 data points, and RH ≥ DRH for n = 996 data points, and (ii) NH_4Cl: RH < DRH for n = 507 data points and RH ≥ DRH for n = 531 data points. It should be noted that the 24 hr average RH during the measurement period was 76.3% and the DRH estimated was 63.2% for NH_4NO_3 and 77.5% for NH_4Cl. These observations on DRH imply that existing humid conditions of the atmosphere during measurement period always favored the formation of NH_4NO_3. Therefore, this could be the possible reason for lack of diurnal variations on a 12 hr basis for NO_3^- ('daytime/nighttime' concentration = 0.96) as explained in Section 3.2. This finding is different from the observations reported in other regions of the World (e.g., Sharma *et al.* (2007) at Kanpur, India; Hu *et al.* (2008) at Pearl River Delta, China; Poulain *et al.* (2011) at Leipzig, Germany).

The measured concentration (ppbv) product (K_m = $[NH_3] \times [HNO_3]$) of HNO_3 and NH_3 was estimated using the measured data and then compared with the theoretical equilibrium constant (K_e) estimated according to the method in Mozurkewich (1993). The 1 hr data (n = 1038) were divided into two cases: (1) ambient RH < DRH, and (2) RH ≥ DRH. For the data sets for Case (1) (n = 42), the plots were made between K_m versus 1000 T^{-1} with the corresponding predicted K_e as shown in Fig. S2. In Fig. S2, it was observed that K_e is always higher than K_m, suggesting that the ambient conditions did not favor the formation of NH_4NO_3 under Case (1). Under Case (2), when DRH ≥ RH (n = 996), the existence of SO_4^{2-} in the deliquescent aerosol particles reduces K_e compared to that of pure NH_4NO_3 solution (Stelson and Seinfeld, 1982b). To incorporate this concept into prediction of equilibrium constant, K_e, the ionic strength fraction (Y) of NH_4NO_3 in $NH_4^+/NO_3^-/SO_4^{2-}$ system, was calculated according to Stelson and Seinfeld, 1982b (Eq (5)):

$$Y = \frac{[NH_4NO_3]}{[NH_4NO_3] + 3 \times [(NH_4)_2SO_4]} \quad (5)$$

K_e* for this system was derived by multiplying K_e with Y. The comparison between K_e* and K_m for Case (2), when DRH ≥ RH, is shown in Fig. 6. It should be noted that we plotted only the daytime and nighttime average values (12 hr) in Fig. 6 for better illustration. On average, K_m was always more than K_e* (95% agreement), suggesting that the meteorological conditions always favor the formation of NH_4NO_3 in Singapore when RH is higher than DRH. Few data points (Fig. 6) having $K_m < K_e$* suggest that NH_4NO_3 might have dissociated under higher temperature during the daytime.

Fig. 7(a) shows the daily variations of K_m and K_e* for NH_4NO_3 and levels of NO_3^- as a function of time series during the measurement period. During most of the days, K_m was larger than K_e*, confirming that the atmospheric conditions were favorable for NH_4NO_3 formation. It could also be concluded that the prevailing levels of NH_3 and HNO_3 in the study area were sufficient to form NH_4NO_3, which can be clearly seen from Fig. 7(a) (comparing K_m and NO_3^- levels). The trends in the conversion of SO_2 into SO_4^{2-} and HNO_3 into NO_3^- were compared with the prevailing temperature and relative humidity (Fig. 7(b) and 7(c)). Finally, temperature plays a significant role in the conversion of SO_2 into SO_4^{2-}, whereas the relative humidity for HNO_3 into NO_3^-.

In an approach similar to NH_4NO_3, we tried to establish relationship between thermodynamics of NH_4Cl. The measured concentration (ppbv) product ($K_m^{'}$ = $[NH_3] \times [HCl]$) of HCl and NH_3 was estimated using the measured data and then compared with the theoretical equilibrium constant ($K_e^{'}$) estimated according to the method in Pio and Horrison (1987a). The 1 hr data (n=1038) were divided into two cases: (1) ambient RH < DRH (n = 507), (2) RH ≥ DRH (n = 531). For Case (1), it was observed that $K_e^{'}$ was always higher than $K_m^{'}$. This indicates that the ambient

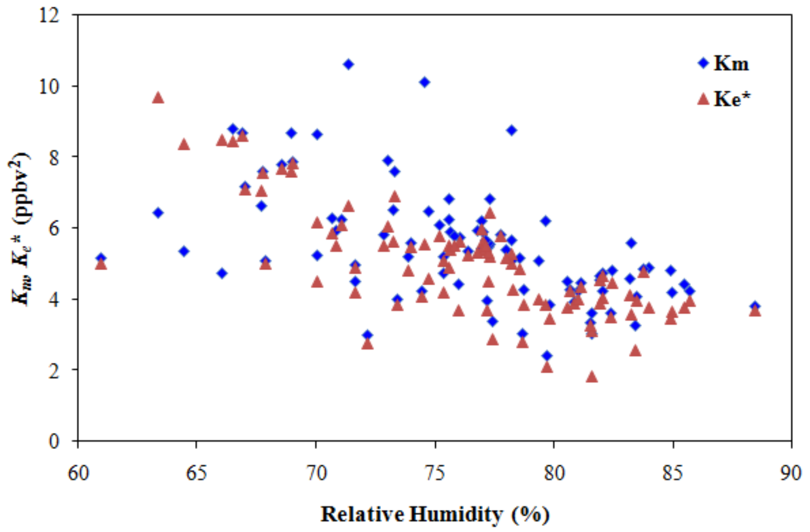

Fig. 6. Comparison of K_m with K_e* when RH was above the DRH of NH_4NO_3.

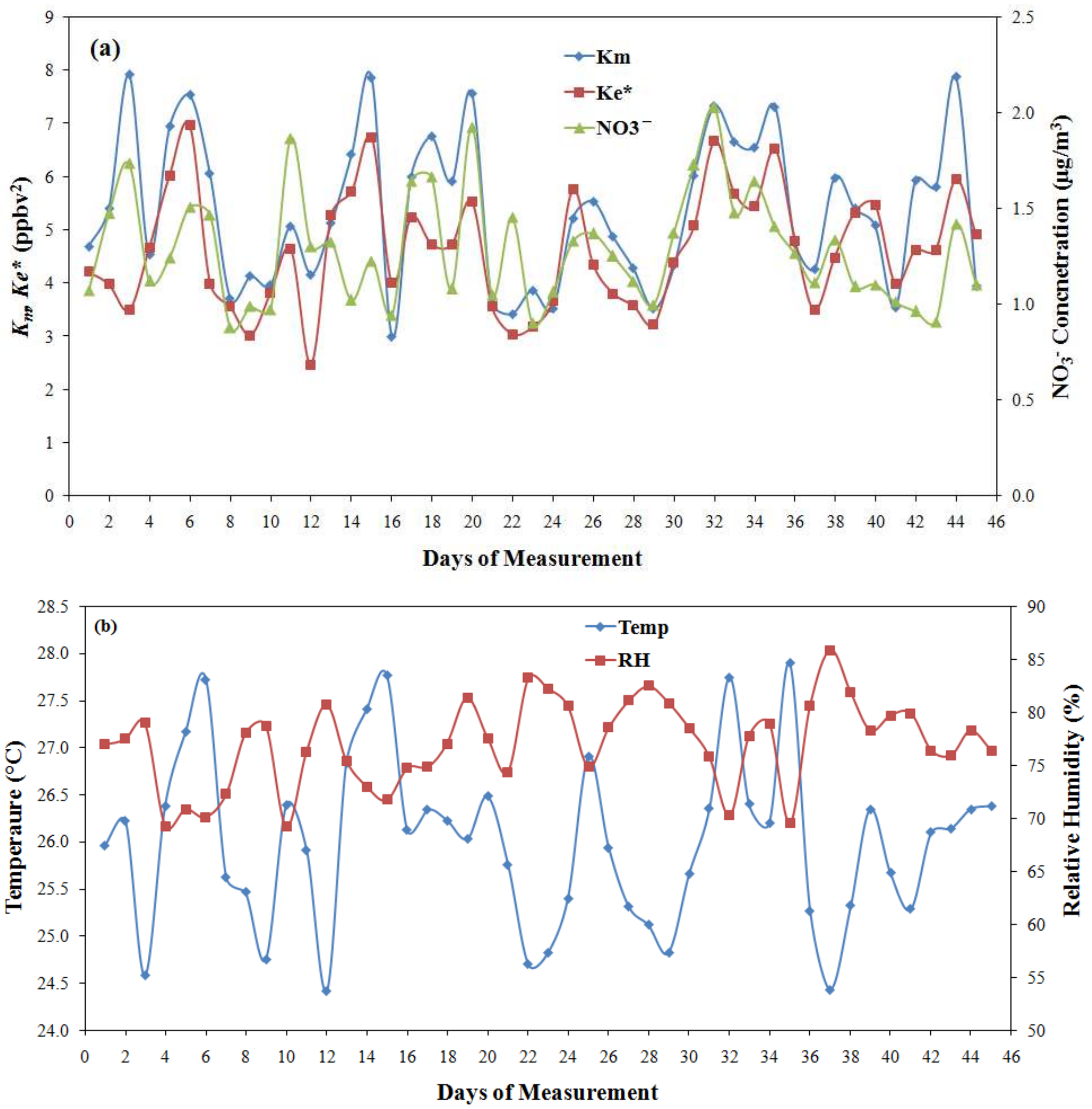

Fig.7. Comparison of (a) nitrate thermodynamics and observed nitrate levels, (b) temperature and relative humidity, and (c) molar ratios of SO_4^{2-} to SO_2 and NO_3^- to HNO_3 on a basis of daily average (24-h) during the measurement period.

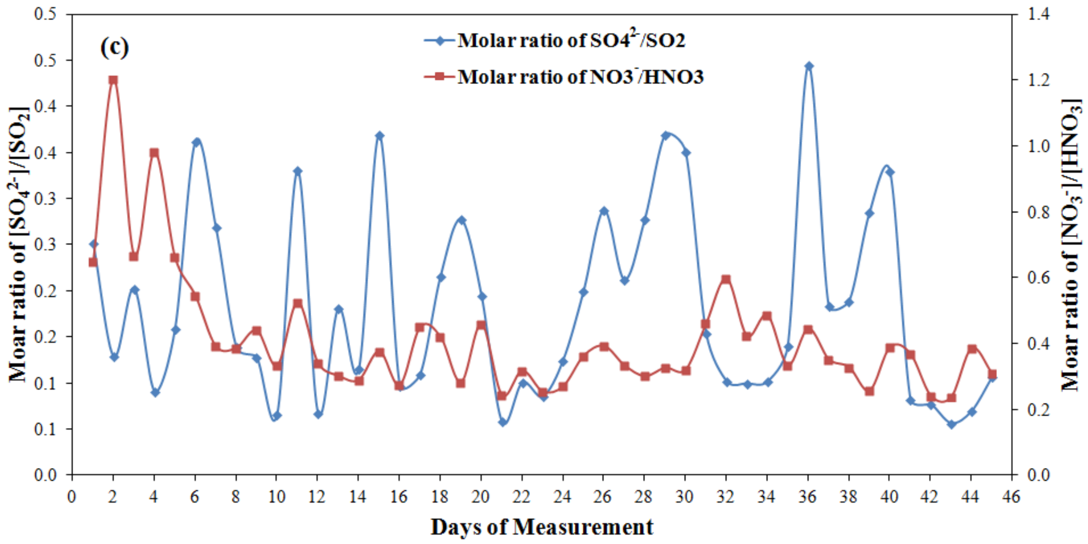

Fig.7. *(continued).*

conditions did not favor the formation of NH_4Cl under Case (1). Under Case (2), it was found that in most of the cases (more than 90% of the data), K_e' was higher than K_m' indicating that the prevailing conditions were not supportive for transformation of HCl into NH_4Cl. The reasons for such observations could be due to: (i) either HCl or NH_3 was not sufficient to drive the reactions in the forward direction, or (ii) the predominance of Cl^- from sea-salt sources may interfere in the process of conversion.

Biomass Burning and SIA formation

In this study, we analyzed two cases to assess the influence of biomass burning on chemical characteristics of $PM_{2.5}$ and gaseous pollutants: (i) Case-1: $K^+ < 0.3$ µg/m³ and (ii) Case-2: $K^+ \geq 0.3$ µg/m³. We classified all 12 hr observations into the two cases and performed a correlation analysis with Minitab 15 English (the results are presented in Table S3). It was clearly observed that K^+ showed higher correlations with Cl^- and NO_3^- under Case-2. Therefore, it can be concluded that under higher K^+ concentration, the formation of Cl^- and NO_3^- can be triggered. Hence, it is a clear indication of the influential role of biomass burning in the formation of chlorides and nitrates in the atmosphere. The observations were compared to some earlier studies: Balasubramanian *et al.* (2003) and Tabazad *et al.* (1998). Balasubramanian *et al.* (2003) had observed the contribution of NO_3^- was more towards total $PM_{2.5}$ mass under smoke hazy conditions than non-hazy conditions. Tabazad *et al.* (1998) had observed that the scavenging of HNO_3 occurred more frequently under smoky conditions with biomass burning. Thus, these two earlier studies supported our hypothesis that biomass burning could have partially triggered nitrate and chloride formation in the study area.

CONCLUSIONS

Acidic gases (SO_2, HONO, HNO_3, HCl), ammonia (NH_3) and water-soluble inorganic ions (SO_4^{2-}, NO_3^-, Cl^-, Na^+, K^+, NH_4^+, Ca^{2+} and Mg^{2+}) in $PM_{2.5}$ were analyzed in Singapore with a short-time interval (1 hr). The results were analyzed to investigate temporal and diurnal variations in $PM_{2.5}$ and their associations and chemical coupling with precursor gases along with the sensitivity of meteorological effects. SO_2, NH_3, HONO, HCl, SO_4^{2-} and Cl^- showed significant diurnal variations at 95% confidence level ($P < 0.05$). However HNO_3, NO_3^-, Na^+, NH_4^+, Ca^{2+} and Mg^{2+} did not show any significant diurnal variations. The peaks of NH_4^+ occurred during the rise in concentrations of NO_3^- and SO_4^{2-}. These peaks of NH_4^+ could be attributed to formation of NH_4NO_3 and $(NH_4)_2SO_4$ during intense traffic emissions of NO_x and more industrial emissions of SO_2. The trace level of NH_3 can neutralize H_2SO_4 and HNO_3 to form significant quantities of $(NH_4)_2SO_4$ and NH_4NO_3 under prevailing atmospheric conditions. In the neutralization process leading to gas-to-particle conversion, this study showed a significant quantity of NH_4^+, SO_4^{2-} and NO_3^- (7.46 µg/m³) in $PM_{2.5}$, which is a matter of concern. Due to the sampling location in the tropical climate, the study area experienced ambient relative humidity to be more than the estimated deliquescence relative humidity of NH_4NO_3 for 96% of the time the total observations were made. These conditions favored the thermodynamics of NH_4NO_3 formation during both daytime and nighttime. The conversion of SO_2 into SO_4^{2-} and HNO_3 into NO_3^- was sensitive to ambient temperature and relative humidity, respectively during the measurement period. Under higher K^+ concentrations (≥ 0.3 µg/m³), the formation of nitrates and chlorides was enhanced. Finally, the charge balance of NH_4^+ and Cl^-, NO_3^-, and SO_4^{2-} ($y = 1.029x + 0.22$ with $R^2 = 0.82$) showed that ammonia-rich conditions prevail in the atmosphere most of the time for fully neutralization of H_2SO_4, HNO_3 and HCl.

ACKNOWLEDGEMENTS

This work is funded by the National Research Foundation (NRF) of Singapore as part of a joint collaboration between the National University of Singapore and Shanghai Jiao Tung University. The authors are grateful to NRF for the financial support (Grant no. R-706-002-101-281) and Metrohm Singapore Pte. Ltd. for providing technical assistance with the MARGA system used in this study.

SUPPLEMENTARY MATERIALS

Supplementary data associated with this article can be found in the online version at http://www.aaqr.org.

REFERENCES

Abas, M.R.B., Rahman, N.A., Omar, N.Y.M.J., Maah, M.J., Samah, A.A., Oros, D.R., Otto, A. and Simoneit, B.R.T. (2004). Organic Composition of Aerosol Particulate Matter during a Haze Episode in Kuala Lumpur, Malaysia. *Atmos. Environ.* 38: 4223–4241.

Acker, K., Spindler, G. and Bruggemann, E. (2004). Nitrous and Nitric Acid Measurements during the INTERCOMP2000 Campaign in Melpitz. *Atmos. Environ.* 38: 6497–6505.

Aneja, V.P., Schlesinger, W.H. and Erisman, J.W. (2009). Effects of Agriculture upon the Air Quality and Climate: Research, Policy, and Regulations. *Environ. Sci. Technol.* 43: 4234–4240.

Baek, B.H. and Aneja, V.P. (2004). Measurement and Analysis of the Relationship between Ammonia, Acid Gases, and Fine Particles in Eastern North Carolina. *J. Air Waste Manage.* 54: 623–633.

Baker, K. and Scheff, P. (2007). Photochemical Model Performance for $PM_{2.5}$ Sulfate, Nitrate, Ammonium, and Precursor Species SO_2, HNO_3, and NH_3 at Background Monitor Locations in the Central and eastern United States. *Atmos. Environ.* 41: 6185–6195.

Balasubramanian, R. and Qian, W.B. (2004). Characterization and Source Identification of Airborne Trace Metals in Singapore. *J. Environ. Monit.* 6: 813–818.

Balasubramanian, R., Qian, W.B., Decesari, S., Facchini, M.C. and Fuzzi, S. (2003). Comprehensive Characterization of $PM_{2.5}$ Aerosols in Singapore. *J. Geophys. Res.* 108: 4523, doi: 10.1029/2002JD002517.

Bari, A., Ferraro, V., Wilson, L.R., Luttinger, D. and Husain, L. (2003). Measurements of Gaseous HONO, HNO_3, SO_2, HCl, NH_3, Particulate Sulfate and $PM_{2.5}$ in New York, NY. *Atmos. Environ.* 37: 2825–2835.

Behera, S.N. and Sharma, M. (2010). Investigating the Potential Role of Ammonia in Ion Chemistry of Fine Particulate Matter Formation for an Urban Environment. *Sci. Total Environ.* 408: 3569–3575.

Behera, S.N. and Sharma, M. (2011). Degradation of SO_2, NO_2 and NH_3 Leading to Formation of secondary Inorganic Aerosols: An Environmental Chamber Study. *Atmos. Environ.* 45: 4015–4024.

Behera, S.N. and Sharma, M. (2012). Transformation of Atmospheric Ammonia and Acid Gases into Components of $PM_{2.5}$: An Environmental Chamber Study. *Environ. Sci. Pollut. Res.* 19: 1187–1197.

Biswas, K., Badar, F., Ghauri, M. and Husain, L. (2008). Gaseous and Aerosol Pollutants during Fog and Clear Episodes in South Asian Urban Atmosphere. *Atmos. Environ.* 42: 7775–7785.

Calvert, J.G., Yarwood, G. and Dunker, A.M. (1994). An Evaluation of the Mechanism of Nitrous Acid Formation in the Urban Atmosphere. *Res. Chem. Intermed.* 20: 463–502.

Charlson, R.J. and Heintzenberg, J. (1995). *Aerosol Forcing of Climate*, Wiley, England, p. 363–382.

Derwent, R., Witham, C., Redington, A., Jenkin, M., Stedman, J., Yardley, R. and Hayman, G. (2009). Particulate Matter at a Rural Location in southern England during 2006: Model Sensitivities to Precursor Emissions. *Atmos. Environ.* 43: 689–696.

Deshmukh, D.K., Deb, M.K., Tsai, Y.I. and Mkoma, S.L. (2011). Water Soluble Ions in $PM_{2.5}$ and PM_1 Aerosols in Durg City, Chhattisgarh, India. *Aerosol Air Qual. Res.* 11: 696–708.

Environmental Protection Division (EPD) Annual Report (2011). National Environmental Agency, Singapore, p. 46.

Finlayson-Pitts, B.J., and Pitts, J.N. (2006). *Chemistry of the Upper and Lower Atmosphere*, 1st Ed., Academic, San Diego, p. 92101–94495.

Gómez-González, Y., Wang, W., Vermeylen, R., Chi, X., Neirynck, J., Janssens, I.A., Maenhaut, W. and Claeys, M. (2012). Chemical Characterisation of Atmospheric Aerosols during a 2007 Summer Field Campaign at Brasschaat, Belgium: Sources and Source Processes of Biogenic Secondary Organic Aerosol. *Atmos. Chem. Phys.* 12: 125–138.

Heo, J.B., Hopke, P.K. and Yi, S.M. (2009). Source Apportionment of $PM_{2.5}$ in Seoul, Korea. *Atmos. Chem. Phys.* 9: 4957–4971.

Hoek, G., Mennen, M.G., Allen, G.A., Hofschreuder, P. and Meulen, T.V. (1996). Concentrations of Acidic Air Pollutants in the Netherlands. *Atmos. Environ.* 30: 3141–3150.

Hu, M., Wu, Z., Slanina, J., Lin, P., Liu, S. and Zeng, L., (2008). Acidic Gases, Ammonia and Water-soluble Ions in $PM_{2.5}$ at a Coastal Site in the Pearl River Delta, China. *Atmos. Environ.* 42: 6310–6320.

Huang, H., Zou, C., Cao, J., Tsang, P., Zhu, F., Yu, C. and Xue, S. (2012). Water-soluble Ions in $PM_{2.5}$ on the Qianhu Campus of Nanchang University, Nanchang City: Indoor-Outdoor Distribution and Source Implications. *Aerosol Air Qual. Res.* 12: 435–443.

Hyer, E.J. and Chew, B.N. (2010). Aerosol Transport Model Evaluation of an Extreme Smoke Episode in Southeast Asia. *Atmos. Environ.* 44: 1422–1427.

Ianniello, A., Spataro, F., Esposito, G., Allegrini, I., Hu, M. and Zhu, T. (2011). Chemical Characteristics of Inorganic Ammonium Salts in $PM_{2.5}$ in the Atmosphere of Beijing (China). *Atmos. Chem. Phys.* 11: 10803–10822.

IPCC: Climate Change (2007). The Physical Science Basis: Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K.B., Tignor, M. and Miller, H.L. (Eds.), Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, p. 996,

Kang, C.M., Lee, H.S., Kang, B.W., Lee, S.K. and Sunwoo, Y. (2004). Chemical Characteristics of Acidic Gas Pollutants and $PM_{2.5}$ Species during Hazy Episodes in Seoul, South Korea. *Atmos. Environ.* 38: 4749–4760.

Kennish, M.J. (1994). *Practical Handbook of Marine Science*, C.R.C. Press, Boca Raton, Fla.

Kim Oanh, N.T., Upadhyay, N., Zhuang, Y.H., Hao, Z.P., Murthy, D.V.S., Lestari, P., Villarine, J.T., Chengchua, K., Co, H.X., Dung, N.T. and Lindgren, E.S. (2006). Particulate Air Pollution in Six Asian Cities: Spatial and Temporal Distributions, and Associated Sources. *Atmos. Environ.* 40: 3367–3380.

Lin, Y.C. and Cheng, M.T. (2007). Evaluation of Formation Rates of NO_2 to Gaseous and Particulate Nitrate in the Urban Atmosphere. *Atmos. Environ.* 41: 1903–1910.

Lin, Y.C., Cheng, M.T., Ting, W.Y. and Yeh, C.R. (2006). Characteristics of Gaseous HNO_2, HNO_3, NH_3 and Particulate Ammonium Nitrate in an Urban City of Central Taiwan. *Atmos. Environ.* 40: 4725–4733.

Lonati, G., Giugliano, M. and Ozgen, S. (2008). Primary and Secondary Components of $PM_{2.5}$ in Milan (Italy). *Environ. Int.* 34: 665–670.

Makkonen, U., Virkkula, A., Mäntykenttä, J., Hakola, H., Keronen, P., Vakkari, V. and Aalto, P.P. (2012). Semi-continuous Gas and Inorganic Aerosol Measurements at a Finnish Urban Site: Comparisons with Filters, Nitrogen in Aerosol and Gas Phases, and Aerosol Acidity. *Atmos. Chem. Phys.* 12: 5617–5631.

Martin, S.T., Schlenker, J.C., Malinowski, A., Hung, H.M. and Rudich, Y. (2003). Crystallization of Atmospheric Sulfatenitrate-ammonium Particles. *Geophys. Res. Lett.* 30: 2102, doi: 10.1029/2003gl017930.

Matsumoto, M. and Okita, T. (1998). Long Term Measurements of Atmospheric Gaseous and Aerosol Species Using an Annular Denuder System in Nara, Japan. *Atmos. Environ.* 32: 1419–1425.

Mozurkewich, M. (1993). The Dissociation Constant of Ammonium Nitrate and Its Dependence on Temperature, Relative Humidity and Particle Size. *Atmos. Environ.* 27A: 261–270.

Muraleedharan, T.R., Radojevic, M., Waugh, A. and Caruna, A. (2000). Chemical Characterization of the Haze in Brunei Darussalam during the 1998 Episode. *Atmos. Environ.* 34: 2725–2731.

Nakajima, T., Higurashi, A., Takeuchi, N. and Herman, J.R. (1999). Satellite and Ground-based Study of Optical Properties of 1997 Indonesian Forest Fire Aerosols. *Geophys. Res. Lett.* 26: 2421–2424.

Pathak, R.K., Wu, W.S. and Wang, T. (2009). 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.

Pathak, R.K., Wang, T. and Wu, W.S. (2011). Nighttime Enhancement of $PM_{2.5}$ Nitrate in Ammonia Poor Atmospheric Conditions in Beijing and Shanghai: Plausible Contributions of Heterogeneous Hydrolysis of N_2O_5 and HNO_3 Partitioning. *Atmos. Environ.* 45: 1183–1191.

Pavlovic, R.T., Nopmongcol, U., Kimura, Y. and Allen, D.T. (2006). Ammonia Emissions, Concentrations and Implications for Particulate Matter Formation in Houston, TX. *Atmos. Environ.* 40: S538–S551.

Pio, C.A. and Harrison, R.M. (1987a). The Equilibrium of Ammonium Chloride Aerosol with Gaseous Hydrochloric Acid and Ammonia under Tropospheric Conditions. *Atmos. Environ.* 21: 1243–1246.

Pio, C.A. and Harrison, R.M. (1987b). Vapour Pressure of Ammonium Chloride Aerosol: Effect of Temperature and Humidity. *Atmos. Environ.* 21: 2711–2715.

Poulain, L., Spindler, G., Birmili, W., Plass-Dülmer, C., Wiedensohler, A. and Herrmann, H. (2011). Seasonal and Diurnal Variations of Particulate Nitrate and Organic Matter at the IFT Research Station Melpitz. *Atmos. Chem. Phys.* 11: 12579–12599.

Qin, Y., Kim, E. and Hopke, P.K. (2006). The Concentrations and Sources of $PM_{2.5}$ in Metropolitan New York City. *Atmos. Environ.* 40: S312–S332.

Remoundaki, E., Kassomenos, P., Mantas, E., Mihalopoulos, N. and Tsezos, M. (2013). Composition and Mass Closure of $PM_{2.5}$ in Urban Environment (Athens, Greece). *Aerosol Air Qual. Res.* 13: 72–82.

Rupakheti, M., Leaitch, W.R., Lohmann, U., Hayden, K., Brickell, P., Lu, G., Li, S.M., Toom-Sauntry, D., Bottenheim, J.W., Brook, J.R., Vet, R., Jayne, J.T. and Worsnop, D.R. (2005). An Intensive Study of the Size and Composition of Submicron Atmospheric Aerosols at a Rural Site in Ontario, Canada. *Aerosol Sci. Technol.* 39: 722–736.

See, S.W., Balasubramanian, R. and Wang, W. (2006). A Study of the Physical, Chemical, and Optical Properties of Ambient Aerosol Particles in Southeast Asia during Hazy and Nonhazy Days. *J. Geophys. Res.* 111, D10S08, doi: 10.1029/2005JD006180.

See, S.W., Balasubramanian, R., Rianawati, E., Karthikeyan, S. and Streets D.G. (2007). Characterization and Source Apportionment of Particulate Matter $\leq$ 2.5 µm in Sumatra, Indonesia, during a Recent Peat Fire Episode. *Environ. Sci. Technol.* 41: 3488–3494.

Seinfeld, J.H. and Pandis, S.N. (2006). *Atmospheric Chemistry and Physics from Air Pollution to Climate Change*, John Wiley, Sons, Inc., New York.

Sharma, M., Kishore, S., Tripathi, S.N. and Behera, S.N. (2007). Role of Atmospheric Ammonia in the Formation of Inorganic Secondary Particulate Matter: A Study at Kanpur, India. *J. Atmos. Chem.* 58: 1–17.

Song, Y., Zhang, Y., Xie, S., Zeng, L., Zheng, M., Salmon, L.G., Shao, M. and Slanina, S. (2006). Source Apportionment of $PM_{2.5}$ in Beijing by Positive Matrix Factorization. *Atmos. Environ.* 40: 1526–1537.

Stelson, A.W. and Seinfeld, J.H. (1982a). Relative Humidity and Temperature Dependence of the Ammonium Nitrate Dissociation Constant. *Atmos. Environ.* 16: 983–992.

Stelson, A.W. and Seinfeld, J.H. (1982b). Thermodynamic Prediction of the Water Activity, NH_4NO_3, Dissociation Constant, Density and Refractive Index for the NH_4NO_3-$(NH_4)_2SO_4$-H_2O System at 25°C. *Atmos. Environ.* 16: 2507–2514.

Stone, E.A., Yoon, S.C. and Sandhauer, J.J. (2011).

Chemical Characterization of Fine and Coarse Particles in Gosan, Korea during Springtime Dust Events. *Aerosol Air Qual. Res.* 11: 31–43.
Stutz, J., Alicke, B. and Neftel, A. (2002). Nitrous Acid Formation in the Urban Atmosphere: Gradient Measurements of NO_2 and HONO over Grass in Milan, Italy. *J. Geophys. Res.* 107: 8192, doi: 10.1029/2001JD000390.
Tabazadel, A., Jacobs, M.Z., Singh, H.B., Toon, O.B., Lin, J.S., Chatfield, R.B., Thakur, A.N., Talbot, R.W. and Dibb, J.E. (1998). Nitric Acid Scavenging by Mineral and Biomass Burning Aerosols. *Geophys. Res. Lett.* 5: 4185–4188.
Tao, J., Ho, K.F., Chen, L., Zhu, L., Han, J. and Xu, Z. (2009). Effect of Chemical Composition of $PM_{2.5}$ on Visibility in Guangzhou, China, 2007 Spring. *Particuology* 7: 68–75.
Trebs, I., Meixner, F.X., Slanina, J., Otjes, R., Jongejan, P. and Andreae, M.O. (2004). Real-time Measurements of Ammonia, Acidic Trace Gases and Water-soluble Inorganic Aerosol Species at a Rural Site in the Amazon Basin. *Atmos. Chem. Phys.* 4: 967–987.
Vedal, S. (1997). Critical Review – Ambient Particles and Health: Lines That Divide. *J. Air Waste Manage.* 47: 551–581.
Weijers, E.P., Schaap, M., Nguyen, L., Matthijsen, J., Denier van der Gon, H.A.C., ten Brink, H.M. and Hoogerbrugge, R. (2011). Anthropogenic and Natural Constituents in Particulate Matter in the Netherlands. *Atmos. Chem. Phys.* 11: 2281–2294.
Wu, Z., Hu, M., Shao, K. and Slanina, J. (2009). Acidic Gases, NH_3 and Secondary Inorganic Ions in PM_{10} during Summertime in Beijing, China and Their Relation to Air Mass History. *Chemosphere* 76: 1028–1035.
Yoshizumi, K. and Hoshi, A. (1985). Size Distributions of Ammonium Nitrate and Sodium Nitrate in Atmospheric Aerosols. *Environ. Sci. Technol.* 19: 258–261.
Zhou, X., Civerolo, K., Dai, H., Huang, G., Schwab, J. and Demerjian, K. (2002). Summertime Nitrous acid Chemistry in the Atmospheric Boundary Layer at a Rural Site in New York State. *J. Geophys. Res.* 107: 4590, doi: 10.1029/2001JD001539.

Received for review, November 26, 2012
Accepted, March 21, 2013