Research Article

The Impact of Nonlocal Ammonia on Submicron Particulate Matter and Visibility Degradation in Urban Shanghai

Roeland Cornelis Jansen, Jianmin Chen, and Yunjie Hu

Shanghai Key Laboratory of Atmospheric Particle Pollution and Prevention,
Department of Environmental Science & Engineering, Fudan University, Shanghai 200433, China

Correspondence should be addressed to Jianmin Chen; jmchen@fudan.edu.cn

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To study the role of submicron particulate matter on visibility degradation in Shanghai, mass concentrations of PM_{10} , secondary inorganic aerosol (SIA) in PM_{10} , and SIA precursor gases were on-line monitored during a 4-week intensive campaign in December 2012. During the campaign, 8 haze periods were identified when on average PM_{10} mass increased to $62.1 \pm 25.6 \mu\text{g}/\text{m}^3$ compared to $30.7 \pm 17.1 \mu\text{g}/\text{m}^3$ during clear weather periods. The sum of SIA in PM_{10} increased in mass concentration during the haze from $14.9 \pm 7.4 \mu\text{g}/\text{m}^3$ during clear periods to $29.7 \pm 10.7 \mu\text{g}/\text{m}^3$ during the haze periods. Correlation coefficients (R^2) of the visibility as function of mass concentrations of SIA species in PM_{10} show negative exponential relations implying the importance of the SIA species in visibility reduction. The important role of ammonia in SIA formation is recognized and demonstrated. Generally, ammonium neutralizes sulfate and nitrate and the molar equivalent ratio of ammonium versus the sum of sulfate and nitrate increases during the haze episodes. Air mass backward trajectories introducing the haze periods show the impact of nonlocal ammonia on visibility degradation in Shanghai.

1. Introduction

The elevated concentrations of haze responsible air pollutants have an adverse impact on human health and the environment [1, 2] and concerns about the adverse effects have led to studies focusing on trends and chemistry of haze episodes in urban China. The megacity Shanghai (24.15 million inhabitants) is located in the Yangtze River Delta (YRD), a cluster of (mega)cities at the east coast of China. The YRD has become of increasing interest to anthropogenic emission studies [3–5] due to large-scale industrial and agricultural activities needed to meet the energy and food demand of the large population. Shanghai has been subject of studies to demonstrate consequences of its urbanization and visibility degradation due to air pollution is one of these consequences [6–9]. In urban areas, elevated concentrations of air pollutants may lead to periods of haze [10, 11] and in Shanghai the phenomenon of haze has become a regular happening [6, 12].

Of the air pollutants, atmospheric aerosol (or particulate matter PM) is mainly responsible for the visibility degradation due to aerosol light scattering [13]. The submicron aerosol size range (described as PM_{10} where the aerosol aerodynamic diameter is equal or less than $1.0 \mu\text{m}$) is highly efficient in scattering of light [2]. Chemically, this size fraction comprises a large mass of secondary inorganic aerosol (SIA) species ammonium (NH_4^+), nitrate (NO_3^-), sulfate (SO_4^{2-}), and chloride (Cl^-) [14]. Huang et al. [15] report a mass fraction of SIA in PM_{10} of 64.4% in Shanghai. The contribution of the particle's SIA fraction in visibility reduction has been studied and concerns mainly scattering of radiation by particulate sulfate and nitrate [16–19]. Moreover SIA species are highly hygroscopic causing increase in the water content of the particles, which enhances the scattering of light [20]. Therefore SIA species have become subject to aerosol studies related to visibility degradation [18, 21–23]. Concentrations of ammonium, nitrate, and sulfate are parameters in models to calculate visibility. The Community

multiscale air quality model (CMAQ) is developed by the USEPA and applied to simulate air quality in North China [24] and to indicate visibility using mass concentrations of SIA species (between organic carbon and elemental carbon) [25–28]. The CMAQ system is used to study formation and transport of air pollutants [29] and has been applied in Asia in modeling studies of air pollutants [24, 30–34]. With the large mass fraction of SIA in PM_{10} and the scattering efficiency of SIA species, it seems crucial to relate the role of PM_{10} to visibility degradation.

Ammonia (NH_3) is the main alkaline gas in the atmosphere [35] and large-scale emissions of ammonia are observed in the YRD [3, 4]. The emission of ammonia from mainly agriculture activities (livestock feeding and fertilizer synthesis) has increased dramatically to meet the food demand of the increasing population of the YRD and the increase in ammonia emission is expected to continue. Ammonia neutralizes acidic trace gases resulting in secondary aerosol containing the ammonium-ion (NH_4^+) [35, 36]. Only ammonia is emitted from the biosphere to the atmosphere; all atmospheric ammonium used to be ammonia [37]. The thermodynamically favored reaction is the neutralization of sulfuric acid (H_2SO_4), which is a product of the oxidation of SO_2 , yielding particulate ammonium sulfate ($(NH_4)_2SO_4(l)$) [38–41]. The reaction between ammonia and nitric acid (HNO_3), which is a product of the oxidation of NO_x , forming particulate ammonium nitrate ($NH_4NO_3(s,l)$) [42, 43] follows. Hydrochloric acid (HCl) contributes to particulate ammonium due to homogeneous reaction with ammonia [44] but atmospheric concentrations of HCl are usually low. Moreover, mass of particulate chloride usually correlates with sodium indicating that the Cl^- is not from the homogeneous reaction of hydrochloric acid with ammonia but originates from sea salt. Due to the role of ammonia in sulfate and nitrate formation and the role of the later species in visibility degradation in urban area, the important role of ammonia is recognized. Erisman and Schaap [45] show the importance of reducing ammonia emissions to achieve lower secondary aerosol concentrations in Europe. Barthelmie and Pryor [46] propose that transport of urban emissions of NO_x and SO_2 over agricultural area with ammonia emissions results in ammonium nitrate and ammonium sulfate formation and consequently higher mass concentrations of PM in agricultural area. Shanghai is ammonia deficient [42, 47] while NO_x and SO_2 are present due to large-scale emissions of traffic and industry. Shanghai is surrounded by agricultural areas where crops are grown and animal farms are situated [3, 4]. Hence it is likely that transport of ammonia from nonlocal sources outside the city of Shanghai is responsible for the elevated concentrations of ammonium, nitrate, and sulfate in Shanghai.

Here we present hourly mass concentrations of SIA species ammonium, nitrate, and sulfate in PM_{10} in Shanghai for 4 weeks of intensive measurements in December 2012. The importance of the presence of ammonium during periods of visibility degradation is demonstrated. To demonstrate that the precursor gas of ammonium, ammonia, is coming from nonlocal sources, backward trajectories of air masses arriving

at the sampling site were computed using the hybrid single-particle Lagrangian integrated trajectory model 4 [48, 49].

2. Methodology

2.1. Location of the Sampling Site and Time of Sampling. Sampling took place in the northeast of Shanghai ($31.3^\circ N$, $121.5^\circ E$) (Figure 1) on the roof (~ 20 m high) of the 4th Teaching Building on the campus of Fudan University. The area around the campus is representative for an urban area due to residential, traffic, and construction activities. Measurements were performed between December 1 and 31, 2012.

2.2. On-Line PM_{10} Inorganic Composition, Related Trace Gas Concentrations and PM_{10} Mass Concentrations. The on-line MARGA ADI 2080 (Applikon-ECN, The Netherlands) was used to acquire hourly concentrations of particulate sodium (Na^+), ammonium (NH_4^+), potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), chloride (Cl^-), nitrate (NO_3^-), and sulfate (SO_4^{2-}) and mixing ratios of gas species ammonia (NH_3), nitric acid (HNO_3), nitrous acid (HNO_2), hydrochloric acid (HCl), and sulfur dioxide (SO_2). MARGA sampled $1 m^3$ of air per hour by means of a Teflon-coated PM_{10} cyclone (URG Co.) situated at the inlet of the instrument. The airflow is volumetric constant and adjusted by a mass flow control system (Bronkhorst HIGH-TECH NL) adjusted according to ambient pressure and temperature. Air temperature inside the measurement station was held constant at $20^\circ C$. Detailed working of MARGA for aerosol and gas measurements can be found elsewhere [50–53] and is only briefly described here. MARGA uses a wet rotating denuder for gas sampling where gases are absorbed on the wall of a liquid coated annulus. Particles make it through this annulus and arrive in the steam-jet-aerosol-collector (SJAC) where a supersaturated environment of steam is created. Steam condenses on the particles and droplets are formed which are collected. Both samples streams (gas and aerosol) are collected by means of a syringe system and analyzed by ion-chromatography. Ammonium salts have been demonstrated to evaporate back to ammonia in the steam chamber of the particle-into-liquid-sampler (PILS) and consequently particulate ammonium concentrations are underestimated between 5 and 20% according to Sorooshian et al., 2006 [54]. Similar studies have not been reported for the MARGA; however, we cannot rule out that ammonium is underestimated due to evaporation in the SJAC. Trebs et al. [55] estimate aerosol loss of $\leq 3\%$ for $PM_{2.5}$ aerosol in MARGA due to nonisokinetic sampling. For gas species sampled by MARGA a “worst case scenario” is calculated using HNO_3 (considered the most difficult gas to sample) and a loss of $\leq 15\%$ is reported.

PM_{10} mass concentrations were obtained from the synchronized hybrid ambient real-time particulate monitor (SHARP Model 5030, Thermo Fisher Scientific). The SHARP is equipped with the intelligent moisture control system (IMR) to regulate humidity levels eliminating moisture effects on mass concentrations that are obtained. The PM_{10} mass

FIGURE 1: Location of the measurement site in Shanghai. Locations 1, 2, and 3 are Yangzhou (NW of Shanghai), Nantong (NNW of Shanghai), and Jiaying (SW of Shanghai).

TABLE 1: Recoveries of the instruments during the measurement period.

Instrument	Valid data (h)	Missing data (h)
MARGA (ADI 2080)	660	84
PM ₁ monitor (SHARP 5030)	744	0
Visibility sensor (Belfort 5000)	743	1
Automatic weather station (Hydro Met)	744	0

concentrations in this study are considered dry mass concentration such as the MARGA results. A Teflon-coated PM₁ cyclone (URG Co.) is situated at the inlet of the instrument.

2.3. Meteorological Data. Visibility was measured using a Belfort Model 5000 sensor. Relative humidity, ambient temperature, ambient pressure, wind speed, and wind direction were monitored with an automatic weather station from Vaisala (HydroMet).

Data recoveries of the instruments are shown in Table 1. The missing data of the MARGA (11%) was due to instrument failure and maintenance.

2.4. Air Trajectory Analysis. To study the aerosol transport characteristics, 3-day air mass backward trajectories were computed using the NOAA hybrid single-particle lagrangian integrated trajectory (HYSPLIT) model 4 from <http://www.arl.noaa.gov/ready/hysplit4.html> [48, 49]. Air masses of two arrival air mass altitudes, namely, 500 and 1000 meters, were used, which represent the average mixed layer height in Shanghai [8, 56, 57].

3. Results and Discussion

3.1. Classification of the Visibility Degradation Episodes with Mass Concentrations of Pollutants. In previous visibility

degradation studies, haze episodes are defined as a continuous period of longer than 4 hours when the visibility is below 10 km while the RH value does not exceed 90% [7, 58, 59]. Low visibility weather can also be caused by high RH ($\geq 90\%$) and is referred to as foggy weather, where the decrease in visibility is in a large extent caused by the amount of water in the air. Data obtained during foggy episodes (RH $\geq 90\%$) as well as data obtained during periods of precipitation are not subject of study here. Time series of the visibility, RH, precipitation, and haze episodes are shown in Figure 2(a). According to the definition of haze described above, 8 haze episodes were identified. The time series of mass concentrations of the particulate species and SIA precursor gasses are shown in Figures 2(b) and 2(c). Details of the events including start and end time, average mass concentrations of SIA species, PM₁ mass concentrations, and SIA precursor gasses are shown in Table 2. Also average data is provided for all haze periods as well as for the foggy periods and clear periods (visibility > 10 km). We will focus on the periods where the visibility is around or less than 10 km while the RH does not exceed 90%.

The hourly PM₁ mass concentrations during the 31 days of measurements averaged $31.9 \pm 21.4 \mu\text{g}/\text{m}^3$ and ranged from 3.3 to $130.6 \mu\text{g}/\text{m}^3$. During the measurement period the average hourly mass concentrations of SIA species in PM₁ were as follows: $[\text{NH}_4^+]$ averaged $4.1 \pm 2.6 \mu\text{g}/\text{m}^3$, $[\text{SO}_4^{2-}]$ averaged $6.0 \pm 2.8 \mu\text{g}/\text{m}^3$, and $[\text{NO}_3^-]$ averaged $5.4 \pm 4.9 \mu\text{g}/\text{m}^3$. The sum of these SIA species averaged $15.5 \pm 9.8 \mu\text{g}/\text{m}^3$ which accounted for $51.1 \pm 12.9\%$ of the PM₁ mass. Sulfate is the most abundant component of the SIA species in PM₁ (22.5 mass%), followed by nitrate (15.1 mass%) and ammonium (13.3 mass%). Sulfate contribution is lower compared to Huang et al. [15] who report a mass fraction in PM₁ in Shanghai of 33.3%, while values for nitrate (16.3%) and ammonium (13.4%) are similar.

The mass concentrations of PM₁ increase significantly during the 8 periods of haze compared to clear weather

TABLE 2: Start and end time, visibility, RH, and average concentrations of aerosol and gas species during the haze, foggy, and clear weather periods.

Start and end time	Vis. (km.)	RH (%)	Aerosol species ($\mu\text{g}/\text{m}^3$)			PM_{10}	Gas species ($\mu\text{g}/\text{m}^3$)		
			NH_4^+	SO_4^{2-}	NO_3^-		NH_3	SO_2	HNO_3
(1) 3/12 12.00–3/12 21.00	8.4	64	6.4	9.7	8.4	48.6	2.5	20.0	0.7
(2) 7/12 22.00–9/12 01.00	7.6	56	11.0	10.9	19.3	93.2	5.1	47.4	2.0
(3) 14/12 12.00–15/12 00.00	6.4	76	8.2	10.5	9.9	65.0	11.8	18.9	0.9
(4) 16/12 15.00–17/12 07.00	6.6	83	4.9	8.5	4.8	31.4	9.5	2.9	0.4
(5) 21/12 09.00–21/12 18.00	5.4	87	4.6	7.4	4.2	44.7	3.7	3.1	0.5
(6) 22/12 09.00–22/12 14.00	7.1	74	7.9	12.6	10.6	54.3	3.2	15.9	0.7
(7) 23/12 07.00–23/12 16.00	9.2	57	9.3	12.6	14.9	65.7	1.1	60.5	2.0
(8) 29/12 23.00–30/12 06.00	6.7	81	5.5	7.9	8.4	48.0	1.7	8.9	0.8
Ave. “haze periods” (94 hours)	7.2	70	7.9	10.1	11.7	62.1	5.4	26.9	1.4
Ave. “foggy” periods (40 hours)	5.4	94	2.9	5.2	2.5	24.2	4.7	3.2	0.4
Ave. “clear” periods (483 hours)	25.6	59	3.9	5.8	5.2	30.7	3.3	23.1	0.9

periods. An average of $30.7 \pm 17.1 \mu\text{g}/\text{m}^3$ during clear periods is measured and an average of $62.1 \pm 25.6 \mu\text{g}/\text{m}^3$ during the haze periods is measured. The sum of SIA species shows a similar trend and increased from an average of $14.9 \pm 7.4 \mu\text{g}/\text{m}^3$ during clear periods to $29.7 \pm 10.7 \mu\text{g}/\text{m}^3$ during the haze periods. This means the mass contribution of SIA to PM_{10} during clear periods averaged $51.0 \pm 12.3\%$ while the mass contribution during the haze averaged $48.2 \pm 7.9\%$. The results imply a relation of PM_{10} and SIA species with the visibility degradation that is observed.

3.2. Correlations between Visibility and Mass Concentrations of PM_{10} Species. The correlations between visibility and PM_{10} mass concentrations of SIA species during clear and haze periods are explored to demonstrate the importance of the SIA species in visibility reduction. The visibility decreases exponentially with increase of PM_{10} mass (Figure 3(a)) and the same trend is observed for SIA species (Figures 3(b), 3(c), and 3(d)). The correlation coefficients (R^2) of the visibility as function of the concentrations are in the order of PM_{10} (0.56) > ammonium (0.52) > sulfate (0.41) > nitrate (0.39). Note that the upper limit of the visibility instrument is 50 km, and the data obtained for mass concentrations during these measurements are not used for the correlation coefficients. Although correlation coefficients are low, it is clear that there is a relation between mass concentrations of PM_{10} solely and SIA mass concentrations in PM_{10} and visibility degradation. Now we demonstrated the importance of PM_{10} and SIA in PM_{10} in visibility measurements and we can focus on time series of the species during decreased visibility. For that the molar equivalent ratio of ammonium versus the sum of sulfate and nitrate and the difference between the expected and observed ammonium in PM_{10} are used.

3.3. Molar Equivalent Ratio of Ammonium to the Sum of Sulfate and Nitrate. The ionic balance,

$$\frac{[\text{NH}_4^+]/18}{([\text{SO}_4^{2-}]/48) + ([\text{NO}_3^-]/62)}, \quad (1)$$

where the species are converted in molar concentrations (mol/m^3), has been applied to study the amount of sulfate and nitrate that has been neutralized by ammonium [42, 60]. Numbers by Pathak et al. [42] for a number of worldwide locations show that particles in urban area are neutralized by ammonium when sulfate and nitrate are low but particles become acidic when ammonium is no longer able to neutralize high mass concentrations of the acidic species sulfate and nitrate. Time series for the molar equivalent ratio of ammonium is shown in Figure 4.

We can now “predict” the concentration of ammonium in PM_{10} assuming that all ammonium is coupled to sulfate and nitrate. For that we apply the following:

$$[\text{NH}_4^+]_{\text{PRED}} = 18 * \left(\left(\frac{[\text{SO}_4^{2-}]}{48} \right) + \left(\frac{[\text{NO}_3^-]}{62} \right) \right) \quad (2)$$

Figure 5 shows the correlation between $[\text{NH}_4^+]_{\text{PRED}}$ and the actual measured NH_4^+ ($[\text{NH}_4^+]_{\text{MEAS}}$), for the entire study period. Data shows very good agreement between the values ($R^2 = 0.97$). The slope of the regression shows an offset of 0.12 which means that, on average, 12 mass% $\text{NH}_4^+_{\text{PRED}}$ is underestimated. This can be explained by ammonium bound to species such as chloride and bisulfate which are not in (2). Contrarily, nitrate and sulfate in (2) may be bound to basic species such as amines [61, 62]. Amines, especially diethyl amine, may compete with ammonia for the acidic species forming amine-salts. Sorooshian et al. [61] report amines concentrations around ~20% of that of ammonium near a bovine source and report that nitrate correlates with amine in PM_{10} . For (2) this would lead to overestimation of $\text{NH}_4^+_{\text{PRED}}$ which means even more than the 12 mass% of the measured ammonium is bound to chloride and bisulfate.

Table 3 shows the results of (1), the predicted NH_4^+ concentrations ($[\text{NH}_4^+]_{\text{PRED}}$), the measured values of NH_4^+ ($[\text{NH}_4^+]_{\text{MEAS}}$), and the differences between predicted and measured NH_4^+ .

On average we observe a value of 1.05 ± 0.11 for (1) during the entire measurement period indicating that there is sufficient ammonium to neutralize nitrate and sulfate and

FIGURE 2: Time series of (a) visibility (km), RH (%), and precipitation (mm/h), (b) mass concentration ($\mu\text{g}/\text{m}^3$) of PM_{10} and SIA species (NH_4^+ , SO_4^{2-} , NO_3^- , and Cl^-), and (c) mass concentration ($\mu\text{g}/\text{m}^3$) of precursor gases (NH_3 , HNO_3 , SO_2 , and HCl) during the study period (December 1–31, 2012) in Shanghai. Gray hatched frames represent the 8 haze episodes.

PM_{10} contains 5 mol% more ammonium than the sum of sulfate and nitrate. Values for (1) during the haze (1.10 ± 0.08) surpassed values of foggy (1.07 ± 0.08) and clear weather (1.05 ± 0.11) periods indicating excess ammonium during the haze periods. For the haze periods 2, 3, and 5 the equimolar balance increases significantly which can at least partly be explained by the elevated concentrations of Cl^- observed

(Figure 2(b)), which may come from organic halides from local industrial sources [42]. The equimolar ratio for haze periods 6, 7, and 8 is far below average and from Figure 2(b) it can be seen that ammonium stays behind sulfate and nitrate concentrations. Periods when ammonia and/or ammonium are high in absolute value (periods 2, 3, 4, and 7 in Table 2) and periods where ammonium surpassed molar equivalent

FIGURE 3: The relationship of particulate species concentration ($\mu\text{g}/\text{m}^3$) and visibility (km) (a) PM_1 , (b) NH_4^+ , (c) SO_4^{2-} , and (d) NO_3^- . Data for rain periods and $\text{RH} > 90\%$ are left out. Data where vis. > 50 km. (upper limit of the instrument) are shown but not used in the R^2 calculation.

values of the sum of sulfate and nitrate (periods 2, 3, and 5) raise interest and need further study.

3.4. The Transport of Nonlocal NH_3 to the Measurement Site. Time series in Figure 2(b) together with the correlations shown in Figures 4 and 5 demonstrate that NH_4^+ , SO_4^{2-} , and NO_3^- in PM_1 follow similar trends. Figure 2(c) demonstrates most of the time NH_3 concentrations show a different trend with SO_2 ($R^2 = 0.17$) and HNO_3 ($R^2 = 0.07$) and this indicates that NH_3 is from a different source than SO_2 and HNO_3 . Traffic and industry in Shanghai are responsible for elevated NO_x and SO_2 [3, 4], and Li et al. [3] show

the numerous point sources of NO_x and SO_2 emission by power plants and industrial activities in Shanghai, hence the assumption that NH_3 is transported to the urban area where it reacts with HNO_3 and H_2SO_4 to form the SIA species. Huang et al. [4] show the spatial allocation of air pollutants emissions with their concentrations over the YRD. For NH_3 emission sources are Yangzhou (NW of Shanghai), Nantong (NNW of Shanghai), and Jiaying (SW of Shanghai) (Figure 1). Figure 6 shows 72-hour air mass backward trajectories for all the haze periods to study the long-distance impact of ammonia on the visibility degradation. Air masses of two arrival altitudes, namely, 500 and 1000 meters, are employed.

FIGURE 4: Time series of the molar equivalent ratio $[\text{NH}_4^+] / ([\text{SO}_4^{2-}] + [\text{NO}_3^-])$ during the study period.

TABLE 3: Average values for the molar equivalent ratio of ammonium to the sum of sulfate and nitrate (1), $[\text{NH}_4^+]_{\text{PRED}}$, $[\text{NH}_4^+]_{\text{MEAS}}$, and the difference between the latter two during the haze, foggy, and clear weather periods.

Start and end time	Equation (1)	$\text{NH}_4^+_{\text{PRED}}$ ($\mu\text{g}/\text{m}^3$)	$\text{NH}_4^+_{\text{MEAS}}$ ($\mu\text{g}/\text{m}^3$)	$\text{NH}_4^+_{\text{MEAS}} - \text{NH}_4^+_{\text{PRED}}$ ($\mu\text{g}/\text{m}^3$)
(1) 3/12 12.00–3/12 21.00	1.06 ± 0.04	6.1	6.4	0.3
(2) 7/12 22.00–9/12 01.00	1.13 ± 0.08	9.7	11.0	1.3
(3) 14/12 12.00–15/12 00.00	1.21 ± 0.04	6.8	8.2	1.4
(4) 16/12 15.00–17/12 07.00	1.07 ± 0.04	4.6	4.9	0.3
(5) 21/12 09.00–21/12 18.00	1.15 ± 0.04	4.0	4.6	0.6
(6) 22/12 09.00–22/12 14.00	1.01 ± 0.02	7.8	7.9	0.1
(7) 23/12 07.00–23/12 16.00	1.03 ± 0.05	9.0	9.3	0.3
(8) 29/12 23.00–30/12 06.00	1.02 ± 0.03	5.4	5.5	0.1
Ave. “haze periods” (94 hours)	1.10 ± 0.08	7.2	7.9	0.7
Ave. “foggy” periods (40 hours)	1.07 ± 0.08	2.7	2.9	0.2
Ave. “clear” periods (483 hours)	1.05 ± 0.11	3.7	3.9	0.2

FIGURE 5: Linear correlation between the predicted amount of ammonium ($= [\text{NH}_4^+]_{\text{PRED}}$) and measured amount of ammonium ($= [\text{NH}_4^+]_{\text{MEAS}}$) for the entire study period ($n = 660$).

FIGURE 6: Continued.

FIGURE 6: Air mass backward trajectories for 500- and 1000-meter altitude arriving in the measurement site at the very beginning of the haze periods (a) 3/12 at 12:00, (b) 7/12 at 22:00, (c) 14/12 at 12:00, (d) 16/12 at 15:00, (e) 21/12 at 09:00, (f) 22/12 at 09:00, (g) 23/12 at 07:00, and (h) 29/12 at 23:00.

Haze periods 2, 3, and 5 are accompanied by a high equimolar ratio of ammonium to the sum of sulfate and nitrate. The air masses arrive in Shanghai by passing over nearby ammonia rich areas (Figures 6(b), 6(c), and 6(e)). Haze periods 6, 7, and 8 are accompanied by lower equimolar ratio and air masses arrive in Shanghai from the North over the East China Sea (Figures 6(f), 6(g), and 6(h)). Air masses arriving in Shanghai before haze periods 1 and 4 come from the West and the NE going party over the East China Sea (Figures 6(a) and 6(d)).

Haze periods 2, 3, and 4 are accompanied by the highest absolute concentrations of ammonia (Table 2) and air masses arrived in Shanghai over nearby ammonia rich areas (Figure 1). Haze periods 6 and 7 are accompanied by high ammonium but relatively low ammonia concentrations indicating that ammonia is not the limiting factor in the aerosol formation. Air masses before this period enter Shanghai over the North Anhui and Shandong provinces.

4. Conclusion

From December 1 to 31 of 2012, 660 hourly samples of secondary inorganic aerosol species ammonium, sulfate, and nitrate together with precursor gasses ammonia, SO_2 , and HNO_3 were obtained to study their role during visibility degradation in urban Shanghai. During the measurement period 8 haze episodes were identified (totaling 94 hours) based on a visibility < 10 km accompanied by an $\text{RH} < 90\%$.

During the entire measurement period the sum of the SIA species in PM_{10} averaged $15.5 \pm 9.8 \mu\text{g}/\text{m}^3$ which accounted for $51.1 \pm 12.9\%$ of the PM_{10} mass. Sulfate mass dominates (22.5%), followed by nitrate (15.1%) and ammonium (13.3%). During haze the sum of SIA species show a similar trend as PM_{10} does and roughly doubles in mass concentrations.

An increase from an average of $14.9 \pm 7.4 \mu\text{g}/\text{m}^3$ during “clear” periods to $29.7 \pm 10.7 \mu\text{g}/\text{m}^3$ during the haze periods is observed for the sum of ammonium, sulfate, and nitrate. This means the mass contribution of SIA to PM_{10} during clear periods averaged $51.0 \pm 12.3\%$ while the mass contribution during haze averaged $48.2 \pm 7.9\%$.

To demonstrate the role of SIA species in the visibility degradation, correlations of visibility versus mass concentrations were studied. The correlation coefficients (R^2) where the visibility is a function of the concentration showed values in the order of PM_{10} (0.56) > ammonium (0.52) > sulfate (0.41) > nitrate (0.39). Correlation coefficients may be low, but figures demonstrate a negative exponential relation between increasing mass concentrations of PM_{10} solely and SIA mass concentrations in PM_{10} and visibility.

The molar equivalent ratio of ammonium versus the sum of sulfate and nitrate shows there is, on average, sufficient ammonium to neutralize sulfate and nitrate during the entire measurement periods and likely ~ 5 mol% ammonium is bound to chloride and bisulfate. The molar equivalent ratio of ammonium versus the sum of sulfate and nitrate increases from 1.05 ± 0.11 for clear weather periods to 1.10 ± 0.08 during haze episodes indicating there is more particulate ammonium than the sum of sulfate and nitrate during haze compared to clear weather. The elevated values can be explained by the formation of ammonium chloride. Correlation between the predicted ammonium (which is the sum of sulfate and nitrate: $\text{NH}_4^+_{\text{PRED}}$) and the actual measured NH_4^+ ($\text{NH}_4^+_{\text{MEAS}}$) for the entire study shows very good agreement between the values ($R^2 = 0.97$) but overestimates $\text{NH}_4^+_{\text{PRED}}$ by $\sim 12\%$.

72-hour air mass backward trajectories for the haze periods are studied to see the long-distance impact of air pollutants on the visibility degradation. Air masses of two

arrival altitudes, namely, 500 and 1000 meters, were computed. The air masses arrive in Shanghai by passing over nearby ammonia rich areas in the YRD where the air masses are injected with ammonia before they reach the site urban Shanghai. Different situations are encountered and ammonia ranged between 1.1 and 11.8 $\mu\text{g}/\text{m}^3$ at the start of a haze period indicating the trajectories affect the mass concentrations of ammonia in urban Shanghai.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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