Atm🙂spheric Pollution Research

Size distribution of water–soluble inorganic ions in urban aerosols in Shanghai

Ye Tao, Zi Yin, Xingnan Ye, Zhen Ma, Jianmin Chen

Shanghai Key Laboratory of Atmospheric Particle Pollution and Prevention (LAP³), Department of Environmental Science and Engineering, Fudan University, Shanghai 200433, China

ABSTRACT

The size distribution of water–soluble inorganic components of urban aerosols in Shanghai was studied. The size–resolved aerosol samples collected by an 8–stage cascade sampler between April and May of 2012 were analyzed by ion chromatography. The ion mass concentrations followed the sequence of SO_4^{2-}>NO_3^- ~NH_4^+>Ca^{2+}>Na^+ ~Cl^->K^+>Mg^{2+}>F^- for each size fraction below 2.1 µm, while the sequence was NO_3^->SO_4^{2-}>Ca^{2+}>NH_4^+>Na^+>Cl^->K^+>Mg^{2+}>F^- for coarse mode particles larger than 3.3 µm. The size distribution in 5 fractions showed that SO_4^{2-}, NO_3^-, and NH_4^+ were generally in the fine mode peaking below 1 µm while Ca^{2+}, Mg^{2+}, Na^+, and Cl^- were bimodally distributed with a second peak larger than 2.1 µm. Back trajectory analyses revealed that the air masses could be classified into three main groups. The total ion concentrations were comparable between the terrestrial and mixing regimes. In the terrestrial regime, fine mode sulfate and nitrate were predominantly associated with ammonium. The excessive sulfate and nitrate over the whole size range might exist in the forms of $Ca(NO_3)_2$ and $CaSO_4$. In the maritime regime, the decrease in SO_4^{2-}, NO_3^-, and NH_4^+ contributed to the improvement in air quality. Besides marine aerosols, local emissions from soil dust and coal combustion were also important sources of sea–salt type ions (i.e., Na^+ and Cl^-).

Keywords: Water–soluble ions, size fraction, secondary aerosols, Yangtze River Delta

Corresponding Author:
Xingnan Ye
☎ : +86-21-65642526
🖷 : +86-21-65642080
✉ : yexingnan@fudan.edu.cn

1. Introduction

China is facing severe challenges from atmospheric pollution, because of the extensive economic development and rapid increase in vehicle population. In 2009, the average daily concentrations of PM_{10} (less than 10 µm in aerodynamic diameter D_P) and SO_2 of the 114 key environmental protection cities reached 87 and 42 µg m^{-3}, respectively. About 300 000 of annually premature deaths were associated with urban air pollution in China (Zhang and Smith, 2007). Under the influence of particle pollution, the annual mean visibility in Beijing and Shanghai decreased ca. 0.8 km per decade during 1973–2007 (Li et al., 2010).

Size–resolved measurements of atmospheric aerosols are of importance, because visibility degradation and adverse health effects are dependent on particle size distribution (Schwartz and Neas, 2000; Seinfeld and Pandis, 2006; Kan et al., 2007). Furthermore, size distribution of chemical compositions can provide relevant information on particle formation mechanism and source apportionment (Wall et al., 1988). Sulfate from seawater is abundant in coarse mode particles while fine mode sulfate is commonly generated by homogeneous or heterogeneous oxidation of SO_2 (Lestari et al., 2003; Tsai et al., 2005). Nitrate produced via the reaction between NH_3 and HNO_3 is predominant in the fine mode particles while coarse mode $NaNO_3$ and $Ca(NO_3)_2$ are mainly from the reactions between HNO_3 and sea salt/soil dust (Cabada et al., 2004). Condensation of secondary organic aerosol mainly affects particle size distribution in the range of 200 and 500 nm while cloud–process extends its impact to 1 000 nm in diameter (Cabada et al., 2004). The fresh aerosols emitted from gasoline vehicles are dominant at 10 nm in contrast to size distribution of diesel vehicle plumes peaking at 30 nm (Kittelson et al., 2004; Yao et al., 2005). Karanasiou et al. (2007) suggested that size distribution of chemical components was also an effective tool for source analysis of trace metals.

There are many studies on chemical characteristics of size–fractionated atmospheric aerosols (Xie et al., 2009; Dordevic et al., 2012; Tsai et al., 2012; Wang et al., 2012). Wang et al. (2012) found that secondary inorganic aerosols in the droplet mode increased sharply during the haze episodes, suggesting the important role of heterogeneous aqueous reactions in the haze formation mechanism.

Shanghai is the economic center of China, as well as the largest megacity in the Yangtze River Delta. To fight with the more and more serious haze pollution, it is crucial to reveal source origin of pollutants and secondary formation mechanisms in this region. However, few studies focused on the size–fractionated chemical compositions in Shanghai (Xiu et al., 2004). To better understand the characteristics of particle components and their source origins, size–fractionated samples have been collected in Shanghai using a cascade sampler in the spring of 2012. Size distributions of water–soluble ions were presented and possible sources were also discussed.

2. Experimental

2.1. Sampling

Sampling was carried out from April 18th to May 23rd in 2012 using an 8–stage Andersen sampler (Thermo Scientific 20–810). The nominal cut–off diameters were 9.0, 5.8, 4.7, 3.3, 2.1, 1.1, 0.7, and 0.4 μm at a flow rate of 28.3 L min^{−1}. The upper cut size for the sampling was assumed to be 30 μm (Karanasiou et al., 2007). The substrate used in the sampler was 80 mm quartz fiber filters (Whatman 1851–865). Before sampling, the pre–heated quartz microfiber filters were weighed on an electrical balance with an accuracy of 0.001 mg (Sartorius BP211D) at 25 °C and 40±2% relative humidity. However, these quartz filters after sampling were weighted at 32 °C by mistake. Our later quality assurance test showed that the weighting error could reach to 55 μg. Thus, the obtained size–fractionated mass concentrations were discarded in this study. The sampling site was on the rooftop (about 20 m high) of a five–story teaching building at the main campus of Fudan University (31.3°N, 121.5°E). The campus was close to the Wujiaochang sub–center of the city, surrounded by a wide mixture of traffic, residential, and industrial emissions. The daily samples were collected for approximately 23 hr, starting at 19:00 local time every day. A total of 25 sets of samples were collected, since there were no samples for rainy days and public holidays. The samples were wrapped with aluminum foil and reserved at −18 °C.

2.2. Analysis of water–soluble ion species

Half of each sample filter was ultrasonically extracted in 10 mL deionized water (18.2 MΩ cm) for 40 min. The extract was analyzed by an ion chromatograph (Dionex ICS–2100A) for major water–soluble inorganic ions. The separation of anions (F^-, Cl^-, SO_4^{2-}, NO_3^-, NO_2^-, and PO_4^{3-}) was accomplished using an IonPac®AS12A analytical column, an AG14 guard column, and an ASRS® 300 anion self–regenerating suppressor. The separation of cations (Li^+, Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}) was accomplished using an IonPac® CS12A analytical column, a CG12A guard column, and a CSRS®300 cation self–regenerating suppressor. The lower and upper limits of detection were 0.5 and 4 μg L^{−1}, respectively. The relative standard deviation of each ion was less than 2% from reproducibility tests. Four blank samples were analyzed with the same process to remove contamination from blank filters and possible sources of pretreatment.

Sampling artifacts can occur with cascade impactors, due to gas–particle interactions, and the dissociation of semi–volatile species (Cheng and Tsai, 1997; Pathak et al., 2009; ten Brink et al., 2009). Decomposition of NH_4NO_3 to gaseous NH_3 and HNO_3 [$NH_4NO_3(s)=NH_3(g)+HNO_3(g)$] due to pressure drop across the filter is the major cause for nitrate artifacts (Zhang and McMurry, 1992; Cheng and Tsai, 1997). Also, nitrate evaporation possibly occurs due to heterogeneous reaction between acidic sulfate and $Ca(NO_3)_2/NaNO_3$ on the filter. Pathak and Chan (2005) suggested an empirical correlation for nitrate artifacts collected on the filter:

$$\text{Nitrate loss (\%)} = 30 \times \left(\ln \frac{[NH_4^+]}{[NO_3^-]} - 1.2 \right) \quad (1)$$

Based on this equation, the nitrate loss in $PM_{2.1}$ was estimated to be less than 3% in our study. The cation–to–anion equivalent ratio is used as a parameter to evaluate the aerosol acidity. Size–segregated acidity is related to the formation, neutralization and heterogeneous atmospheric processes, which can give insight into the mechanisms in different aerosol modes (Kerminen et al., 2001; Yao et al., 2007; Cheng et al., 2011).

3. Results and Discussion

Figure 1 illustrates the measured size–fractionated ion mass concentrations in contrast to the official PM_{10} concentrations reported (http://www.envir.gov.cn). To focus on fine particulate matter pollution, coarse mode particles above 3.3 μm were incorporated into one size fraction. Among the 25 sets of samples, the total ion mass concentrations ranged from 22.3 to 96.7 μg m^{−3}, with an average of 48.1 μg m^{−3}. The highest concentration was observed on 7th May when the official daily PM_{10} loading was 210 μg m^{−3}, four times above the World Health Organization Air Quality Guidelines of 50 μg m^{−3} (24 hr average). In contrast, the concentration of total anions and cations was only 22.3 μg m^{−3} on 20th May when the official daily PM_{10} loading was 28 μg m^{−3}. In this work, we approximately defined the ion concentrations in $PM_{2.1}$ and TSP (total suspended particles) by ignoring the contribution of particles below 0.4 μm, since the lower cut off diameter of the sampler is 0.4 μm. The ion concentration ratio of $PM_{2.1}$ to TSP varied in the narrow range of 52–70%.

Figure 2 illustrates the equivalent balance between inorganic anions and cations among the 25 sets of samples. The ion balance was expressed by the sum of the equivalent concentration (μeq m[−3]) of anions (F^-, Cl^-, SO_4^{2-}, NO_3^-, NO_2^-, and PO_4^{3-}) to cations (NH_4^+, Na^+, K^+, Li^+, Mg^{2+}, and Ca^{2+}) for each size fraction of each sample. The linear fit between the equivalent concentrations of total anions and total cations displayed a correlation coefficient (r) of 0.97 and a slope (k) of 0.96. Obviously, the slope of the linear regression fairly coincided with the theoretical value (equivalent ratio 1.0). The fact that the cations were well balanced by the anions suggested that the aerosols were fully neutralized as a whole. This feature was in agreement with Wang et al. (2013) who reported that the equivalent ratio of cations to anions in $PM_{2.5}$ was slightly larger than 1.0. Fully neutralized aerosol was reported widely in different areas all over the world (Salcedo et al., 2006; He et al., 2012; Shon et al., 2012). In contrast, Wang et al. (2006) suggested that the $PM_{2.5}$ in Shanghai ten years ago was slightly acidic while coarse mode particles were alkaline.

Table 1 summarizes the mass concentrations of major water–soluble inorganic ions for different size fractions.

Table 1. Mass concentrations of major inorganic ions (ng m^{−3}) in each size fraction over the whole observation

Species	0.4<D_p<0.7 μm	0.7<D_p<1.1 μm	1.1<D_p<2.1 μm	2.1<D_p<3.3 μm	D_p>3.3 μm	Total	$PM_{2.1}$/TSP
NH_4^+	776.0±383.7	2 768.3±1 236.4	2 533.6±1 397.2	436.6±284.3	506.1±386.1	7 020.6±3 302.0	0.87
Na^+	180.4±263.2	285.7±198.8	410.3±375.5	234.1±135.8	622.4±331.8	1 732.9±771.1	0.51
K^+	47.5±68.8	166.2±150.6	184.6±134.7	78.7±73.6	94.6±79.9	571.6±407.5	0.70
Mg^{2+}	21.6±14.4	39.2±17.5	62.1±24.7	59.1±22.4	114.1±34.4	296.1±78.2	0.42
Ca^{2+}	367.7±285.6	691.8±353.7	887.2±414.3	686.6±288.5	1 375.7±696.5	4 009±1 474.9	0.49
F^-	17.7±39.6	38.3±72.6	16.2±26.3	22.2±43.1	73.7±97.1	168.1±200.7	0.43
Cl^-	179.2±133.5	274.8±196.6	292.0±205.4	283.1±195.7	527.4±262.5	1 556.5±696.0	0.48
NO_3^-	792.3±395.5	2 685.8±1 387.9	2 910.0±1 767.8	1 423.8±633.9	3 683.0±2 109.9	11 495.0±5 395.2	0.56
SO_4^{2-}	2 403.8±937.9	7 039.2±3 240.5	6 790.1±3 784.2	2 298.5±777.1	2 641.5±906.9	21 173.1±8 384.1	0.77
Σions	4 786.2±2 522.2	13 989.3±6 854.6	14 086.1±8 130.1	5 522.7±2 454.4	9 638.5±4 905.1	48 022.3±20 870	0.68