

Characteristics of Major PM_{2.5} Components during Winter in Tianjin, China

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Abstract

Fine particles were simultaneously collected at an urban, industrial and coastal site in Tianjin, China from December 28, 2006 to January 31, 2007 to investigate the chemical characteristics of major PM_{2.5} components during an annually occurring season of high pollution. Water-soluble inorganic ions, organic carbon (OC) and elemental carbon (EC) were analyzed. Daily average concentrations of PM_{2.5} ranged from 61.5-566.8 µg/m³ with an average of 223.0 µg/m³. The sum of the measured species accounted for about 60% of the PM_{2.5} mass with organic aerosols and sulfates being the two largest contributors. Total carbon (OC + EC) constituted 23.3%, 25.5% and 19.2%, and secondary ionic species (SO₄²⁻, NO₃⁻ and NH₄⁺) constituted 27.6%, 19.0% and 25.9% of PM_{2.5} at the urban, industrial and coastal sites, respectively. The PM_{2.5} composition in the industrial area was influenced by local industrial emission sources. About 80% of the total carbon existed in the form of OC, and the average OC/EC ratios were 4.5, 5.6 and 4.8 at the urban, industrial and coastal sites, respectively. Secondary organic carbon (SOC), estimated by the minimum OC/EC ratio, accounted for about 37.2% ~ 50.3% of total OC. High Cl⁻ concentrations averaging 9.3 µg/m³ were found, which mostly originated from anthropogenic sources, rather than from sea-salt aerosols.

Keywords: PM_{2.5}; Chemical composition; Water-soluble ions; Organic carbon; Elemental carbon.

INTRODUCTION

Tianjin, located about 120 km southeast of

Beijing, is the largest coastal city in northern China, and has a total population of over 10 million and an area of 11919.7 km². As an industrial municipality, the major industries in Tianjin include electronics, automobile, petrochemical, metallurgy, biomedical, and

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new energy, among others. Coal is the main energy source supplying the city with 66% of its total energy consumption. Crude oil was 30% in 2005 (Statistics Year Book of Tianjin, 2006). The number of vehicles exceeds 1.2 million and the number of private cars is growing quickly at a rate of nearly 20% per year. The increasing fuel usage and continuous population growth have brought about serious air pollution problems to the city. Particulate matter (PM) has been observed as the principal pollutant. During “The Tenth Five-Year Period” (2001-2005), the annual averages of PM₁₀ ($d_p \leq 10 \mu\text{m}$) for Tianjin all exceeded China’s Class 2 PM₁₀ standard of 100 $\mu\text{g}/\text{m}^3$, and is classified as one of the most polluted regions in China (China Environmental Situation Report, 2001-2005, SEPA). Resuspended dust, coal and biomass burning, traffic and industrial emissions all contribute to PM pollution in Tianjin (Cao *et al.*, 2006; Tao *et al.*, 2006; Bi *et al.*, 2007).

Fine particulate matter ($d_p \leq 2.5 \mu\text{m}$, PM_{2.5}) has received worldwide attention for its adverse impacts on human health, visibility degradation and global climate change (Laden *et al.*, 2000; Ramanathan *et al.*, 2001; Watson, 2002). In the meantime, China is of great concern for its large population, number of automobiles, and tremendous increases in energy consumption. In order to understand the status of fine particle pollution and its impacts on air quality in China, comprehensive research studies have been carried out in the most-developed cities like Beijing, Shanghai, Guangzhou and Hong Kong, as well as in Taiwan (He *et al.*, 2001;

Ye *et al.*, 2003; Hagler *et al.*, 2006; Louie *et al.*, 2006; Lin *et al.*, 2008). High loadings of fine PM have been observed in urban regions of China. It has also been observed that air pollution is often regional in nature (Street *et al.*, 2007).

Prior studies of PM in Tianjin have focused mainly on total suspended particulate, while a few were related to PM_{2.5} (Zelenka, *et al.*, 1994; Zhang and Friedlander, 2000; Cao *et al.*, 2007). Study of the chemical characteristics of PM_{2.5} is necessary in understanding the sources of air pollutants as well as in establishing efficient strategies to control aerosol pollution problems. For this reason, a one-month field sampling campaign was conducted during the highly polluted heating season at three representative sites of Tianjin. The main objectives of this paper are to report the PM_{2.5} mass concentration and the chemical composition with focus on water-soluble ions and carbonaceous aerosol, as well as to evaluate the likely sources of major chemical species during winter.

EXPERIMENTAL

PM_{2.5} Sampling

Sampling was simultaneously conducted at three sampling sites (as shown in Fig. 1): (1) An urban site, which is located in a commercial-residential area of the downtown and approximately 100 m away from a heavy-traffic road; (2) An industrial site, which is about 14 km northeast to the urban site, located in a suburban district with a large number of industrial emission sources,

including chemical factories (e.g., producing fertilizer, spice, dye), machinery and automotive fitting manufacturing, electronics, etc.; (3) A coastal site about 50 km southeast of downtown and adjacent to the Tianjin Harbor.

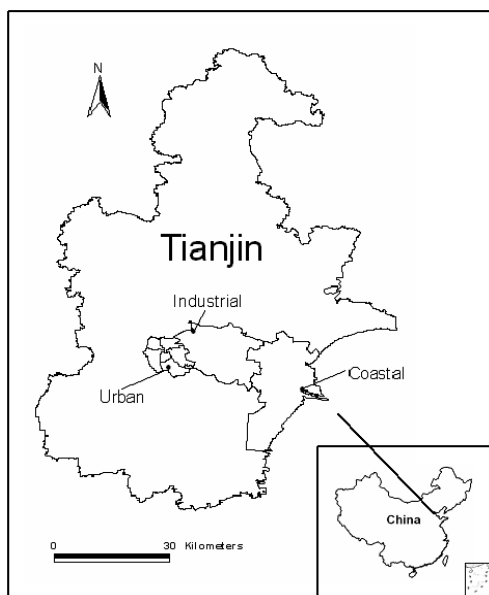


Fig. 1. Three sampling sites in Tianjin: (1) urban site, a type of commercial-residential site also influenced by traffic emissions; (2) industrial site, located in a suburban district with a large number of factories; (3) coastal site, located in the Tanggu District and adjacent to Tianjin harbor.

Medium-volume $PM_{2.5}$ samplers (Wuhan Tianhong Intelligence Instrumentation Facility, model TH-150A II, flow rate: 100 L/min) were employed for aerosol sampling. The performance of this sampler was verified by a Federal Reference Method (FRM) sampler (PQ200, BGI, Inc.). The difference between the two types of samplers was less than 5% for the $PM_{2.5}$ mass concentrations. The 24-h $PM_{2.5}$

samples were collected on 90 mm quartz-fiber filters (2500 QAT-UP, Pall Life Sciences, USA), which were pre-heated to remove residual carbon at 800°C for 3h before using. After stabilizing in a controlled desiccator for 48h, all the filters were weighed before and after sampling by an electronic microbalance with 1 μg sensitivity (Mettler Toledo, Switzerland). The exposed filters were stored at about -18°C before chemical analysis. Sampling was carried out on an every-3rd-day schedule between December 28, 2006 and January 31, 2007, and a total of 36 valid samples were obtained. Field blank filters were also collected and the sample results were corrected by the average of the blank concentrations.

Chemical Analysis

Chemical analysis included water-soluble inorganic ions (Cl^- , NO_3^- , SO_4^{2-} , Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+}), OC and EC. Ion chromatography (IC, Dionex120) was used for the analysis of anion and cation concentrations. One-fourth of each filter was extracted with 10 mL deionized water in an ultrasonic bath for 20 min. The water extract was filtered twice through 0.2 μm microporous membranes and the filtrate was injected into the IC with polypropylene syringes. The IonPac AS14 and IonPac CS12A were used as the anion and cation analytical columns, respectively. The eluent for anion analysis was a 3.5 mM carbonate (Na_2CO_3)/1.0 mM bicarbonate (NaHCO_3) solution. The eluent for cation analysis was a 20 mM methanesulfonic acid solution. The relative standard deviation (SD)

of each ion was less than 5% for the reproducibility test. Quality assurance testing was made with a reference standard known concentration, which was typically within 10% of the standard value.

The OC and EC of the samples were analyzed by the IMPROVE thermal/optical reflectance (TOR) method with DRI Model 2001 Thermal/Optical Carbon Analyzer. Briefly, OC and EC are determined by heating a small sample punch under different temperature and oxidation environments. OC is defined as all carbon that evolves from the sample when heated up to 550°C in a 100% helium atmosphere. EC is defined as all carbon that evolves from the sample when heated up to 800°C in an atmosphere of 2%O₂/98% He after the organic carbon has been removed. The carbon that evolves at each temperature is converted to methane and quantified with a flame ionization detector (FID). The correction for pyrolysed organic carbon (POC) is made by continuously monitoring the filter reflectance throughout an analysis cycle. The portion of the elemental carbon peak corresponding to POC is assigned to the organic fraction. Principals and details of the analytical procedures are available elsewhere (Chow *et al.*, 1993; Cao *et al.* 2003).

RESULTS AND DISCUSSION

PM_{2.5} Mass Concentrations and Meteorological Conditions

During the field study, ambient temperature ranged from -5.9°C to 2.4°C with a mean value of -1.9°C, the relative humidity (RH)

was from 27-82% with a mean value of 50%, and wind speed was from 0.7 m/s to 7.0 m/s with a mean value of 2.0 m/s. There is no notable precipitation recorded in the observation period. The wind direction was mostly from west-northwest-north and no clear relationship was found between PM concentrations and wind direction.

To identify the origin and transport pathway of air masses, two-days-backward air trajectories were calculated at the altitudes of 100 m for every sampling day using a HYSPLIT_4 model developed by NOAA/ARL (<http://www.arl.noaa.gov/>). Most air parcels arriving in Tianjin originated from either Mongolia or Russia and then passed through Inner Mongolia, Shanxi and Hebei provinces. In addition, short trajectories that come from the local areas over Tianjin were also observed. Air-mass trajectories show that atmosphere in Tianjin is a superposition of transported polluted air on locally produced pollutants.

A statistical summary of the 24-h average concentrations of PM_{2.5} chemical species is given in Table 1. The daily PM_{2.5} mass concentrations ranged from 61.5 to 566.9 µg/m³ with an overall average of 223.0 µg/m³ which was more than six times of the US NAAQS daily PM_{2.5} Standard of 35 µg/m³. The severe PM_{2.5} pollution in winter can be attributed to increased emissions from heating sources and poor atmospheric dispersion. The level of PM_{2.5} in the city is obviously increased in comparison with that (averaged 179.4 µg/m³) in 2003 (Cao *et al.*, 2007); however, PM₁₀ exhibited a decreasing trend.

Table 1. The mean and standard deviation (SD) of PM_{2.5} chemical species at the urban, industrial and coastal sites in Tianjin (measured from December 28, 2006 to January 31, 2007) ($\mu\text{g}/\text{m}^3$).

| Site | Statist | PM _{2.5} | Na ⁺ | NH ₄ ⁺ | K ⁺ | Mg ²⁺ | Ca ²⁺ | Cl ⁻ | NO ₃ ⁻ | SO ₄ ²⁻ | OC | EC |
|------------------------------|---------|-------------------|-----------------|------------------------------|----------------|------------------|------------------|-----------------|------------------------------|-------------------------------|------|-----|
| Urban (n=12) ^a | Mean | 206.6 | 1.0 | 11.3 | 3.3 | 0.1 | 0.9 | 8.5 | 17.1 | 40.9 | 41.4 | 8.0 |
| | SD | 143.4 | 0.6 | 8.8 | 2.4 | 0.1 | 0.5 | 5.1 | 16.9 | 45.5 | 29.8 | 2.4 |
| Industrial (n=12) | Mean | 248.2 | 1.1 | 11.5 | 4.5 | 0.2 | 1.4 | 11.1 | 13.6 | 32.5 | 61.5 | 9.3 |
| | SD | 170.8 | 0.6 | 8.9 | 3.6 | 0.1 | 0.9 | 6.1 | 16.7 | 42.4 | 33.9 | 2.1 |
| Coastal (n=12) | Mean | 215.6 | 1.0 | 10.9 | 4.2 | 0.2 | 1.7 | 8.6 | 16.8 | 45.6 | 36.7 | 6.9 |
| | SD | 193.9 | 0.6 | 11.7 | 3.3 | 0.1 | 1.0 | 7.2 | 20.1 | 75.7 | 33.2 | 2.7 |
| 3 sites average | | 223.0 | 1.0 | 11.2 | 4.0 | 0.2 | 1.3 | 9.3 | 15.9 | 39.7 | 46.0 | 8.0 |

^a Number of samples

This signifies the role of fine particle in air pollution problems.

The daily variation of PM_{2.5} concentrations was as high as a factor of 8, corresponding to the strong meteorological variations in winter. The maximum concentrations of most PM_{2.5} species at all sites appeared on January 3, 2007 with low wind speed (1.4 m/s) and the highest RH (82%). Such conditions are usually favorable for pollutant accumulation and transformation. On January 6, 2007 when the wind speed reached as high as 7.0 m/s and RH appeared a low value (27%), PM_{2.5} concentration dropped to the lowest level (61.5 $\mu\text{g}/\text{m}^3$) during the entire sampling period. It can be explained that the wind strength can influence the atmospheric cleaning effect through dispersion of pollutants, and RH plays an important role in secondary aerosol formation (McHenry and Dennis, 1994; Blando and Turpin, 2000).

Inorganic Water-Soluble Ions

Water-soluble ions comprise a large portion of ambient particles and play an important role in the atmosphere. On average, the 8 inorganic

water-soluble ions contributed about one-third of PM_{2.5} mass. SO₄²⁻, NO₃⁻, NH₄⁺ and Cl⁻ were observed as the dominant ionic species, accounting for 48.0%, 19.2%, 13.6% and 11.3% of the total mass of inorganic ions, respectively.

The three-site average concentrations of major secondary species, SO₄²⁻, NO₃⁻ and NH₄⁺, were 39.7, 15.9 and 11.2 $\mu\text{g}/\text{m}^3$, respectively, accounting for about 13.1%, 5.7% and 4.7% of the PM_{2.5} mass. High wintertime SO₄²⁻ concentrations have been commonly observed in China due to enhanced SO₂ emissions from coal combustion for residential heating (He *et al.*, 2001; Hagler *et al.*, 2006). The sum of SO₄²⁻, NO₃⁻ and NH₄⁺ was 69.4, 57.6 and 73.3 $\mu\text{g}/\text{m}^3$ at the urban, industrial and coastal site, accounting for 27.6%, 19.0% and 25.9% of the PM_{2.5} mass, respectively. The abundance of secondary ions was comparatively low at the industrial site due to the higher industrial emissions.

Correlation analysis was performed for each of the secondary species among the three sites. The urban and coastal data exhibited good correspondences ($R^2 > 0.9$), and also presented

Table 2. Matrix of correlation coefficient among water-soluble ions.

| | SO ₄ ²⁻ | NO ₃ ⁻ | Cl ⁻ | K ⁺ | Na ⁺ | NH ₄ ⁺ | Ca ²⁺ | Mg ²⁺ |
|-------------------------------|-------------------------------|------------------------------|-----------------|----------------|-----------------|------------------------------|------------------|------------------|
| SO ₄ ²⁻ | 1.00 | 0.85 | 0.41 | 0.66 | 0.82 | 0.95 | -0.08 | 0.51 |
| NO ₃ ⁻ | | 1.00 | 0.64 | 0.74 | 0.95 | 0.94 | -0.03 | 0.72 |
| Cl ⁻ | | | 1.00 | 0.55 | 0.71 | 0.63 | 0.34 | 0.69 |
| K ⁺ | | | | 1.00 | 0.73 | 0.72 | 0.05 | 0.66 |
| Na ⁺ | | | | | 1.00 | 0.93 | 0.12 | 0.74 |
| NH ₄ ⁺ | | | | | | 1.00 | -0.04 | 0.61 |
| Ca ²⁺ | | | | | | | 1.00 | 0.54 |
| Mg ²⁺ | | | | | | | | 1.00 |

correlations with industrial data with R² 0.8~0.9. These observations suggest that secondary aerosol pollutants are widespread over the city and may be from either regional formation or long-range transport.

As illustrated in Table 2, there is strong linear correlation between SO₄²⁻, NO₃⁻ and NH₄⁺ with a correlation coefficient R² of 0.95 and 0.94, which indicated that these species are associated in the same particulate system, in the likely form of NH₄NO₃, ([NH₄]₂SO₄) or NH₄HSO₄. Particulate phase NH₄⁺ concentrations can be calculated using the stoichiometric ratios of the different compounds and compared with actual measurements (Chow *et al.*, 1996).

In Fig. 2. ammonium is calculated from nitrate and sulfate, assuming that all nitrate is in the form of NH₄NO₃ and all sulfate is in the form of either (NH₄)₂SO₄ (i.e., calculated ammonium = 0.38 × sulfate + 0.29 × nitrate) or NH₄HSO₄ (i.e., calculated ammonium = 0.192 × sulfate + 0.29 × nitrate). It shows reasonable agreement when NH₄HSO₄ is assumed.

However, the calculated ammonium from NH₄HSO₄ is still higher than the measured

ones, suggesting that fine particles collected during the study period were either more acidic, or that sulfate and nitrate were associated with cations other than ammonium, such as sodium and potassium.

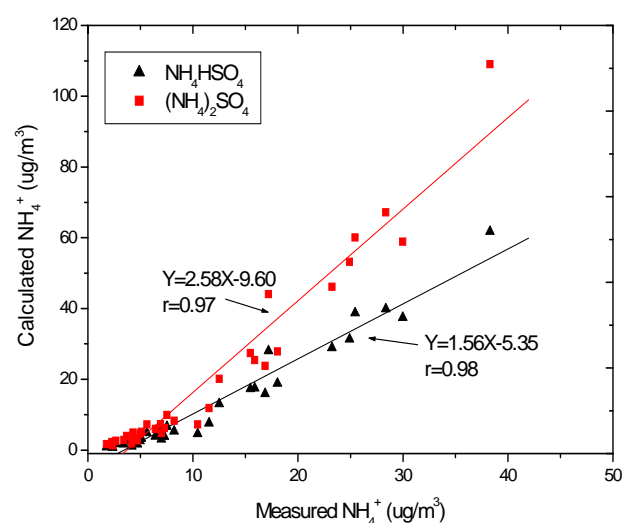


Fig. 2. Comparison between calculated and measured ammonium.

The ion balance, expressed by the equivalent concentration (μeq/m³) ratio of cations to anions (Σ⁺/Σ⁻, C/A), was calculated from the measured ionic species to evaluate the acidity of fine particles. It was found that for most of the samples, C/A ratios were lower than unity with the mean value of 0.61, 0.78

and 0.66 at the urban, industrial and coastal site, respectively. Considering that the partition of semivolatile species (i.e., NH_4^+ , NO_3^-) is driven toward particulate phase in cold season (Park *et al.*, 2004), ammonium evaporation is not a major problem. So, the cation deficiency was probably due to hydrogen that was not considered in the calculation, which indicated that the wintertime $\text{PM}_{2.5}$ in Tianjin was acidic and would do more harm to public health and the ecological environment.

The mass ratio of $\text{NO}_3^-/\text{SO}_4^{2-}$ can be used as an indicator of the relative importance of mobile vs. stationary sources (Arimoto *et al.*, 1996). High $\text{NO}_3^-/\text{SO}_4^{2-}$ ratios were found in vehicle-predominant regions. However, lower ratios (0.3~0.5) have usually been found in China because of the wide use of sulfur-containing coal (Yao *et al.*, 2002). The ratio measured in this study varied between 0.17 and 0.76 with an average of 0.47, which was comparable to the values in Beijing (0.49; Wang *et al.*, 2005) and Shanghai (0.43; Yao *et al.*, 2002). The $\text{NO}_3^-/\text{SO}_4^{2-}$ ratios imply that coal-combustion related emissions are more responsible for air pollution than vehicle exhaust during winter in China.

It is reported that temperature plays an important role in the gas-phase oxidation of SO_2 to sulfate, and low temperature in cold season could inhibit secondary formation of SO_4^{2-} (Wang *et al.*, 2005). Sulfur oxidation ratio defined as $\text{SOR} = n\text{-SO}_4^{2-}/(n\text{-SO}_4^{2-} + n\text{-SO}_2)$ can be used as an indicator of the secondary transformation processes. In this study, *SOR* was calculated for those urban

samples due to availability of SO_2 concentration data. The average value of *SOR* was 0.15, higher than the criteria of 0.1 used for identification of secondary aerosol formation (Ohta and Okita, 1990), which clearly shows secondary formation of SO_4^{2-} from SO_2 occurred in winter. Aqueous phase reaction or in-cloud process, as well as long-range transport, might be the important pathways of SO_4^{2-} formation in winter (Yao *et al.*, 2002).

High Cl^- concentrations with the average value of $9.3 \mu\text{g}/\text{m}^3$ were observed in wintertime $\text{PM}_{2.5}$ in Tianjin, which was higher than those in other urban environments. In an attempt to estimate whether the chlorine was from sea salt, the Cl^-/Na^+ concentration ratio in aerosol samples was compared with that of sea water. The Na^+ concentrations were generally lower than $1.0 \mu\text{g}/\text{m}^3$ during the sampling period. The average Cl^-/Na^+ ratios were 8.15, 10.53 and 8.66 at the urban, industrial and coastal sites, respectively; while it was only 1.17 for sea water (Hu *et al.*, 2002). The enrichment of Cl^- resulted from anthropogenic emissions, such as coal combustion and industrial discharge (Watson and Chow., 2001; Wang *et al.*, 2005). The concentrations of Cl^- were about 30% higher at the industrial site than those at the other two sites, pointing to industrial Cl^- emissions from local chemical industries. For example, the fertilizer factory, producing potassium sulfate from the reaction of potassium chloride and sulfuric acid, can release considerable amounts of hydrochloric acid into the atmosphere. The contribution of sea salt aerosol to $\text{PM}_{2.5}$ was minor. Further

research is needed to understand sources of Cl⁻ of in Tianjin.

The tracer of biomass burning, K⁺, was also found in high concentrations. The three-sites average of K⁺ was 4.0 µg/m³ and accounted for about 7.3% of the total inorganic ions, higher than the winter values of 2.5 µg/m³ and 4% in Beijing during 2001-2003 (Wang *et al.*, 2005). Burning of straw to produce energy is a common practice in rural Tianjin. In addition, Zelenka *et al.* (1994) found an enrichment of potassium for the coal burning profile and ascribed it to the practice of burning vegetative scrap along with the coal by local residents. So, biomass burning may be an important source of PM_{2.5} in Tianjin.

The sum of Ca²⁺, Na⁺ and Mg²⁺ was only 2.5 µg/m³ and constituted 6.9% of the total inorganic ions, indicating the minor impacts of soil dust and sea salt aerosols.

Organic Carbon and Elemental Carbon

Fine carbonaceous matter is emitted from most combustion processes, and consists of two major components: EC and OC. The latter, which is a matter of great concern because of possible mutagenic and carcinogenic effects, can be directly emitted from sources (primary OC) or produced from atmospheric reactions involving gaseous organic precursors (secondary OC) (Turpin and Huntzicker, 1995). EC, also referred to as black carbon or soot, originates primarily from direct emissions of particles. As the principal light-absorbing particulate specie, EC plays an important role in visibility reduction and the aerosol radiative forcing (Jacobson, 2001).

Carbonaceous species are among the major components of fine particles in Tianjin. The average concentrations of OC were 41.4, 56.8, 36.7 µg/m³, and of EC were 8.0, 9.0, 7.0 µg/m³ at the urban, industrial and coastal site, respectively. Total carbon (OC + EC) accounted for 23.3%, 25.5% and 19.2% of PM_{2.5} mass at the three sites, respectively. The highest loadings of carbonaceous aerosol observed in the industrial area could be primarily ascribed to the many organic-related factories, which can emit considerable organic pollutants during operation. Another possible factor may be related to emissions from nearby single-story residential houses for migrant workers where honeycomb briquettes and crude coal (both with very low combustion efficiency) were the main fuel for heating and cooking. The relatively low level of carbonaceous aerosol at the coastal site could be explained by less industrial and residential emissions there.

The comparison of OC and EC concentrations and OC/EC ratios with other urban measurements are shown in Table 3. The OC concentration in Tianjin is lower than that in Xi'an, but higher than those in other cities, pointing out serious OC pollution in Tianjin. The EC concentration is comparable to those of most domestic cities, but much higher than those of foreign cities. OC and EC concentrations in this study were consistent with those measured in Tianjin by Cao *et al.* (2007). Table 3 clearly shows the severity of carbonaceous aerosol pollution in urban regions of China. Residential and industrial emissions were identified as the major

Table 3. Comparison of OC, EC concentrations ($\mu\text{g}/\text{m}^3$) and OC/EC ratios with results from other cities^a.

| Location | Sampling period | OC | EC | OC/EC | Reference |
|----------------------|---------------------|------|------|-------|--------------------------------|
| Tianjin ^b | Dec.2006-Jan. 2007 | 41.4 | 8.0 | 4.8 | This study |
| Beijing | Dec.-Feb. 1999 | 31.5 | 11.1 | 2.8 | He <i>et al.</i> (2001) |
| Shanghai | Dec.-Feb. 1999 | 17.6 | 8.1 | 2.2 | Ye <i>et al.</i> (2003) |
| Guangzhou | Jan.-Feb. 2002 | 22.6 | 8.3 | 2.7 | Cao <i>et al.</i> (2003) |
| Xi'an | Dec.2003-Feb. 2004 | 61.9 | 12.3 | 5.1 | Cao <i>et al.</i> (2005) |
| Tianjin | Jan. 2003 | 38.9 | 8.5 | 4.5 | Cao <i>et al.</i> (2007) |
| Chongju, Korea | Jan.-Feb. 1996 | 5.0 | 4.3 | 1.2 | Lee and Kang (2001) |
| Seoul, Korea | Mar.2003-Feb. 2005 | 10.2 | 4.1 | 2.5 | Kim <i>et al.</i> (2007) |
| Chattanooga, USA | Jan.-Feb. 2001 | 5.1 | 2.4 | 2.1 | Tanner <i>et al.</i> (2004) |
| Helsinki, Finland | July 2000-July 2001 | 3.0 | 1.2 | 2.5 | Viidanoja <i>et al.</i> (2002) |

^a Measurement method: IMPROVE-TOR was used by all the studies except Helsinki with NIOSH-TOT.

^b The urban site

contributors to carbonaceous aerosol emission in China (Cao *et al.*, 2006), while traffic emission is the predominant contributor in foreign cities. In addition, more semi-volatile organic compounds tend to coagulate and adsorb on the particle surface under low temperature.

Strong correlation between OC and EC was observed for the winter $\text{PM}_{2.5}$ samples with the correlation coefficient R^2 of 0.80, indicating the existence of common dominant sources for the two carbon components. High OC/EC ratios were observed in Tianjin compared with those in other cities (Table 3). The enrichment of OC can be explained by the combination of higher contributions of sources with high OC/EC ratio (e.g., coal combustion, biomass burning; Cao *et al.*, 2005) and secondary organic aerosol formation. The average OC/EC ratios were 4.8, 5.9 and 4.5 at the urban, industrial and coastal sites, respectively. Elevated OC/EC ratios observed at the industrial site might be related to the emission

pattern of higher OC and lower EC emission rates of local sources.

A primary OC/EC ratio of 2.2 (Turpin and Huntzicker, 1991) or 2.0 (Chow *et al.*, 1996) was usually regarded as an indication of the presence of secondary organic particles. All the OC/EC ratios except one in this study exceeded 2, implying the possible presence of secondary organic carbon (SOC). In general, SOC formation is reduced in winter compared to summer due to low temperature and decreased actinic fluxes. However, the low mixing layer height coupled with enhanced emission of organic precursors in winter is in favor of SOC formation (Strader *et al.*, 1999). Duan *et al.* (2005) reported that even in winter, the SOC contribution to OC in ambient aerosol was as high as 40% in Beijing.

The amount of SOC was roughly estimated using the minimum OC/EC ratio method put forward by Castro *et al.* (1999), that is:

$$OC_{\text{sec}} = OC_{\text{tot}} - EC \times (OC/EC)_{\text{min}} \quad (1)$$

where OC_{sec} is the secondary OC, OC_{tot} is the total OC, and $(OC/EC)_{min}$ is the minimum ratio of ambient aerosol. In this study, the minimum ratio of OC/EC was 1.8, 2.6 and 2.1 at the urban, industrial and coastal sites, respectively, and all occurred on the same day when the meteorological conditions (e.g., unstable air mass, low RH, lack of sun) were not favorable for SOC formation. The calculated SOC were 27.1, 33.6 and 22.2 $\mu\text{g}/\text{m}^3$ accounting for 50.3%, 45.7% and 37.2% of the total OC at the urban, industrial and coastal sites, respectively. The contributions of SOC to OC are comparable to those in Beijing (40%, Duan *et al.*, 2005), Guangzhou (49.6%, Cao *et al.*, 2003), Kaohsiung City (40%, Lin and Tai, 2001), Helsinki (50%, Viidanoja *et al.*, 2002), but higher than those in San Joaquin Valley of California (20%) (Strader *et al.*, 1999), Birmingham (17%, Castro *et al.*, 1999). It should be noted that the potential SOC estimated by the minimum OC/EC ratio method has large and unquantifiable uncertainty because of the large uncertainties in OC and EC determination as well as in the primary OC/EC ratios (Turpin and Huntzicker, 1995; Watson *et al.*, 2005).

Chemical Composition of $PM_{2.5}$

Table 4 lists the mass percentages of major components in $PM_{2.5}$ at each site. The amount of organic matter (OM) is estimated by multiplying OC by 1.4 to account for other atoms, such as oxygen (O), hydrogen (H), and nitrogen (N) in organics. On average, the seven components explained about 60% of the

$PM_{2.5}$ mass, of which major ionic species (sum of SO_4^{2-} , NO_3^- , Cl^- and NH_4^+) accounted for 23-31%, while carbonaceous species (OM + EC) accounted for 25-34%. The unresolved fraction, averaging about 33-41% of the total $PM_{2.5}$ mass, could be attributed to crustal material and other trace species. Water associated with inorganic salts might account for part of the unidentified mass, especially in the presence of sulfates more acidic than ammonium bisulfate (Hand *et al.*, 2000). As Fig. 3 shows, the unresolved fraction increases as $PM_{2.5}$ mass loadings decrease. For instance, on January 6, 2007 the lowest $PM_{2.5}$ concentrations in this study, the unidentified fraction even reached to 74.5%, but the abundance of Ca^{2+} (an indicator for crustal material) increased significantly. Elevated $PM_{2.5}$ concentrations were largely driven by carbonaceous and secondary ionic components, which mainly resulted from anthropogenic combustion sources.

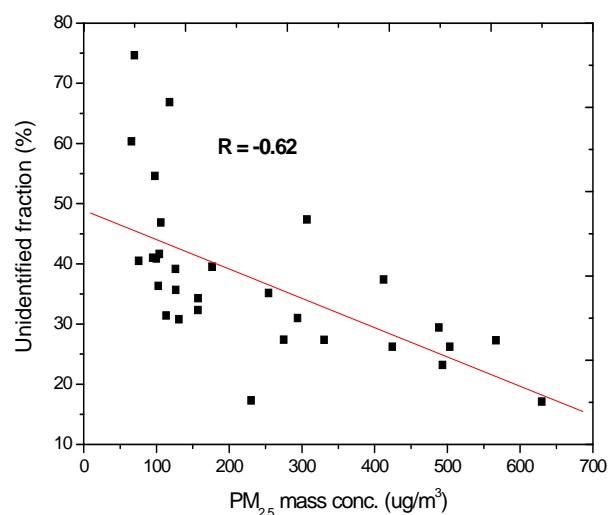


Fig. 3. Comparison of the total $PM_{2.5}$ concentration and the unresolved fraction of $PM_{2.5}$

Table 4. Mass percentages (%) of major components in PM_{2.5} at three sites of Tianjin

| Site | 1.4 × OC | EC | SO ₄ ²⁻ | NO ₃ ⁻ | NH ₄ ⁺ | Cl ⁻ | Other ions ^a | Total |
|---------------|----------|-----|-------------------------------|------------------------------|------------------------------|-----------------|-------------------------|-------|
| HX-urban | 25.8 | 4.8 | 15.5 | 6.4 | 5.1 | 4.1 | 2.9 | 64.6 |
| DL-industrial | 29.7 | 4.2 | 9.8 | 4.2 | 4.6 | 4.4 | 4.1 | 61.0 |
| TG-coastal | 20.9 | 4.2 | 13.4 | 6.0 | 4.5 | 4.0 | 4.3 | 57.3 |

^aSum of K⁺, Na⁺, Ca²⁺, Mg²⁺

Of all the species, organic matter was the single largest component accounting for 20.9-29.7% of PM_{2.5} mass, presenting such spatial distribution as industrial > urban > coastal. The contributions of EC (4.2-4.8%) at the three sites were almost at the same level, indicating that EC might not be influenced strongly by those local factors at various types of sampling sites. Three secondary ionic species; i.e., SO₄²⁻, NO₃⁻ and NH₄⁺, constituted 9.8-15.5%, 4.2-6.4% and 4.5-5.1% of the fine mass, respectively. Both SO₄²⁻ and NO₃⁻ presented the lowest level in the industrial area. On the whole, PM_{2.5} chemical composition was similar among the sites despite the differences found in organic and several ionic species between industrial, urban, and coastal areas.

CONCLUSIONS

Severe PM_{2.5} pollution was observed during winter in Tianjin with the monthly average concentration of 223.0 µg/m³. Consistent with other urban measurements, organic aerosols and sulfates were the two largest contributors to PM_{2.5} mass concentration in Tianjin. Major species contributing to fine mass included SO₄²⁻, NO₃⁻, NH₄⁺, Cl⁻, OC and EC, and the measured species explained about 60% of the

PM_{2.5} mass.

On average, water-soluble inorganic ions constituted about one third of PM_{2.5} mass concentration, of which SO₄²⁻ accounted for 37.1% of the total mass of inorganic ions. Organic matter, estimated by 1.4 × OC, was the most predominant component, accounting for about 25.8%, 29.7% and 20.9% of PM_{2.5} mass at the urban, industrial and coastal site, respectively. The levels of EC were similar for all the sites, with a relatively low contribution (4.4%) to fine mass. Secondary organic carbon, estimated by minimum OC/EC ratio method, constituted about 37.2-50.3% of the total OC. Elevated PM_{2.5} episodes were largely driven by carbonaceous aerosol and secondary ionic components, both related to fossil fuel combustion, which signifies the role of controlling anthropogenic combustion sources in fine particle abatement. Further studies of the sources and unidentified components of PM_{2.5} are under investigation.

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