

Seasonal variations of water-soluble ions in PM₁₀ at a WMO/GAW station in the Yangtze River Delta, China

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Abstract. In order to understand the seasonal levels, formation mechanism and atmospheric chemical behaviours of water-soluble ions of PM₁₀ in the Yangtze River Delta (YRD) region, aerosol samples were collected from January 2nd to December 28th, 2017 at a WMO/GAW regional background station in Lin'an. The concentrations of PM mass and nine water-soluble inorganic ions were obtained. The annual average concentration of PM₁₀ was 59.9±33.9 μg m⁻³, lower than those reported in previous studies, indicating air quality of YRD region was improved. Nine water-soluble inorganic ions was accounted for 30.2-45.1% of the total PM mass, while ammonium (NH₄⁺), sulfate (SO₄²⁺), as well as nitrate (NO₃⁻) were the major ions which contributed 86.3% to total ions. The NO₃⁻ concentration was lowest in summer but highest in winter, suggesting it was likely influenced by thermodynamics. The levels of SO₄²⁻ in spring and winter were related to photochemical reaction and regional transportation. Except for the SNA, Ca²⁺ was highest in four seasons likely due to sand storm and road fugitive dust. The annual mean ratio of [NO₃⁻]/[SO₄²⁻] was nearly to 1, indicating mobile and stationary sources were equally important in Lin'an. The mean nitrogen oxidation ratio (NOR) and sulfur oxidation ratio (SOR) were 0.22±0.13 and 0.41±0.13, respectively, suggesting secondary formation was significant in the atmosphere at the background station of YRD region.

1 Introduction

Since the strong link between air pollution and adverse health effects has been revealed, the elevated atmospheric particulate matters especially for inhalable particles (aerodynamic diameter less than 10 μm, PM₁₀) have become a public concern due to their abilities to induce chronic respiratory inflammation and acute cardiovascular disease, as well as the obvious impacts on haze formation and climate change [1, 2]. In past few decades, the economically developed regions in China, such as the Jing-Jin-Ji area and the Yangtze River Delta (YRD) region, etc., have suffered from serious air quality which are mainly caused by PM emissions [3-5]. The chemical composition plays very important roles in atmospheric behaviors of PM like visibility degradation and secondary aerosol formation. For instance, carbonaceous species and water-soluble ions are considered as the main factors leading visibility reducing. Meanwhile, the three major ions (ammonium (NH₄⁺), sulfate (SO₄²⁺), as well as nitrate (NO₃⁻) have been identified as the tracers for secondary inorganic aerosols in previous studies of source apportionment [6]. Huang et al. (2012) has demonstrated that secondary inorganic aerosols (SNA) was one of the three sources related with fog haze in the YRD region during field observations, rest of which were biomass burning and long-range transport [7].

In this study, annual PM₁₀ samples were collected at a WMO/GAW regional background station in the YRD region, and the concentration of water-soluble ions were analyzed to understand their seasonal variations, formation mechanism and atmospheric chemical behaviors. The main aim of our work is to find out the existence forms of SNA and their relationships to indicate the characteristics of emission sources, which would provide a scientific basis for policy making and atmospheric environmental studies.

2 Experiment and methods

2.1 Sampling site

The samples were collected at a WMO/GAW background station in Yangtze River Delta, located in Lin'an, Hangzhou, China (119.73°E, 30.3°N). The station was in the top of a hill and surrounded by some farmland. A small town (about 200 inhabitants) and a little factory with production of charcoal from bamboo were seated in the north of Lin'an station (about 210 km southwest of the megacity Shanghai and 50 km west of the Hangzhou, the capital city of Zhejiang Province). The average annual temperature and humidity in Lin'an was 17.8°C and 70.3%, which enjoys sub-tropical monsoon climate with abundant rainfall.

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In this study, a total of 98 PM₁₀ samples were collected on quartz filter (Whatman, 47 mm, USA) in 2017 using a Minivol™ aerosol sampler (Airmetrics, USA) with flow rate of 5L min⁻¹. Two samples were collected in every week and the sampling period of all samples was 24h from 9:00 to 9:00 in next day, while one field blank filter was collected in every month. Before sampling, all quartz filters were prebaked for 6h at 600°C in muffle furnace to remove the organics. The filters were balanced in a controlled relative humidity (30-40%) and temperature (23-26°C) environment before and after sampling for 48h prior to weighing on an analytical microbalance (Mettler-MX5, Mettler Toledo, Switzerland) with a 10 µg limit of detection. All filters were reserved in the refrigerator for -18°C until analyzed.

2.2 Water-soluble ions analysis and quality control

Nine water-soluble inorganic ions (Cations: F⁻, Cl⁻, SO₄²⁻, NO₃⁻; Anions: Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺) were analyzed in this study. A quarter of filter was put in a vial with 10 mL ultrapure water (18.2MΩ), sonicated for 30 min in an ice-water bath and filtered with a 0.22 µm Teflon filter to remove the insoluble materials. Then extract was analyzed by ion chromatography (ICS-5000+, Dionex, USA). Cations determination was performed by the Dionex IonPac CS12A column using 20 mmol L⁻¹ Methyl sulfonic acid as the eluent at a 1mL min⁻¹ flow rate and detected by a CSRS 300 suppressor system. Anions determination was performed by Dionex IonPac AS11HC column using 30 mmol L⁻¹ NaOH as the eluent at a 1mL min⁻¹ flow rate and detected by a AERS suppressor system. The method limit of detection (LOD) was shown in Table 1.

Table 1 The LODs for measurement ions (µg mL⁻¹)

F ⁻	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻		
0.0009	0.0016	0.005	0.0088		
Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	
0.0002	0.0013	0.0004	0.0004	0.0007	

3 Results and discussions

3.1 The level of PM₁₀

The daily concentration of PM₁₀ and measurement water-soluble ions were shown in Fig. 1(a). The annual mean mass concentration of PM₁₀ in 2017 at Lin'an background station was 59.9±33.9 µg m⁻³, lower than the Second Grade National Ambient Air Quality Standard (NAAS-2012) of China (70 µg m⁻³) and the earlier study reported in this sampling site, e.g., 79 µg m⁻³, 64 µg m⁻³, 71 µg m⁻³ and 70 µg m⁻³ from 2010 to 2014, respectively [8]. Zhang et al. (2015) also observed the level of PM₁₀ in 2013 was lower than the value in 2016 at Lin'an

station [9]. These results showed the air quality of YRD region was enhanced in recent years.

In this study, four seasons were identified, e.g., spring (March 1st to May 31st), Summer (July 1st to August 31st), autumn (September 1st to November 30th) and winter (December 1st to February 28th). During observation, the highest PM₁₀ mass concentration was observed in winter, with an annual average value of 72.9±41.4 µg m⁻³, followed by 61.8±27.1 µg m⁻³ in spring, 58.16±35.67 µg m⁻³ in autumn and 42.17±23.12 µg m⁻³ in summer, respectively. So, Lin'an had the most serious particle pollution in winter and slightest particle pollution in summer, which was in accordance with Beijing, Shanghai and Guangzhou reported in previous researches [5, 10, 11]. Compared with other seasons, the lowest concentration in summer may be due to the abundant shower (about one third days) and the actions of rainwash can remove some particles suspended to the atmosphere [12].

3.2 Characteristics of water-soluble inorganic ions

3.2.1 Mass concentrations

During sampling period, the annual average concentration for total water-soluble ions was 23.6±10.2 µg m⁻³, which accounted for 39.38% of the total PM₁₀ mass, indicating that ions was an important component of PM₁₀. This annual mean level in this study was lower than that observed in other cities of YRD region, e.g., Nanjing (46.0 µg m⁻³ in 2010) and Jinhua (35.27±24.16 µg m⁻³ in 2018) [13, 14]. The secondary inorganic ions (SO₄²⁻, NO₃⁻, NH₄⁺), with the mean concentrations of 8.07±4.92, 8.48±7.96 and 3.81±3.80 µg m⁻³, respectively, were the major ions in PM₁₀, accounting for 34.21, 35.92 and 16.13%, respectively, in total measurement water soluble ions. The fraction of Ca²⁺ (6.04%), Na⁺ (2.66%), Cl⁻ (2.65%) and K⁺ (1.35%) were low compared with SNA. The other two ions, Mg²⁺ (0.16±0.13 µg m⁻³) and F⁻ (0.08±0.16 µg m⁻³), each had small contribution (<0.70%) to total ions (Fig. 1(b) and (c)).

3.2.2 Seasonal variations

As shown in Fig. 1(b) and (c), the levels of chemical compositions in PM₁₀ were various in four seasons, which was associated with different meteorological conditions (temperature, relative humidity, wind speed and direction, etc.), the intensity of emission sources, as well as pollution transportation [3, 15, 16]. The total measurement ions contributed for 30.24-45.08% to PM₁₀ in four seasons. On the seasonal basis, the levels of F⁻, Cl⁻, SO₄²⁻, NO₃⁻ and NH₄⁺ were highest in winter. The Na⁺, Mg²⁺, and Ca²⁺ peaked in autumn, while K⁺ peaked in spring.

Compared with other three seasons, the mass concentration of NO₃⁻ and NH₄⁺ were lowest in summer, mainly due to easily decomposition of NH₄NO₃ and formation of gaseous NH₃ and HNO₃ with the highest temperature (27.72±3.76°C). The high level of SO₄²⁻

appeared in winter and spring, with mean value of $11.81 \pm 7.06 \mu\text{g m}^{-3}$ and $8.15 \pm 3.52 \mu\text{g m}^{-3}$, respectively (Fig. 1(c)). This phenomenon was also observed in previous study in this station. The high level of SO_4^{2-} was because of the photochemical reaction with both high concentration of ozone and sulfur dioxide in spring and was influenced by emissions of regional transportation in winter [3]. Except for the SNA ions, The level of Ca^{2+} was highest in every seasons, likely

from sand storm and road fugitive dust owe to the roadway in the southwest (about 50m) of the station [17]. Besides, the highest concentration of Cl^- peaked in winter and was 1.5-4.3 times of other three seasons, mainly due to coal combustion and heating emissions [3]. For the K^+ , it showed weak seasonal variation at Lin'an station likely because of the continuous emissions from the charcoal factory (pyrolysis the bamboo) during sampling period.

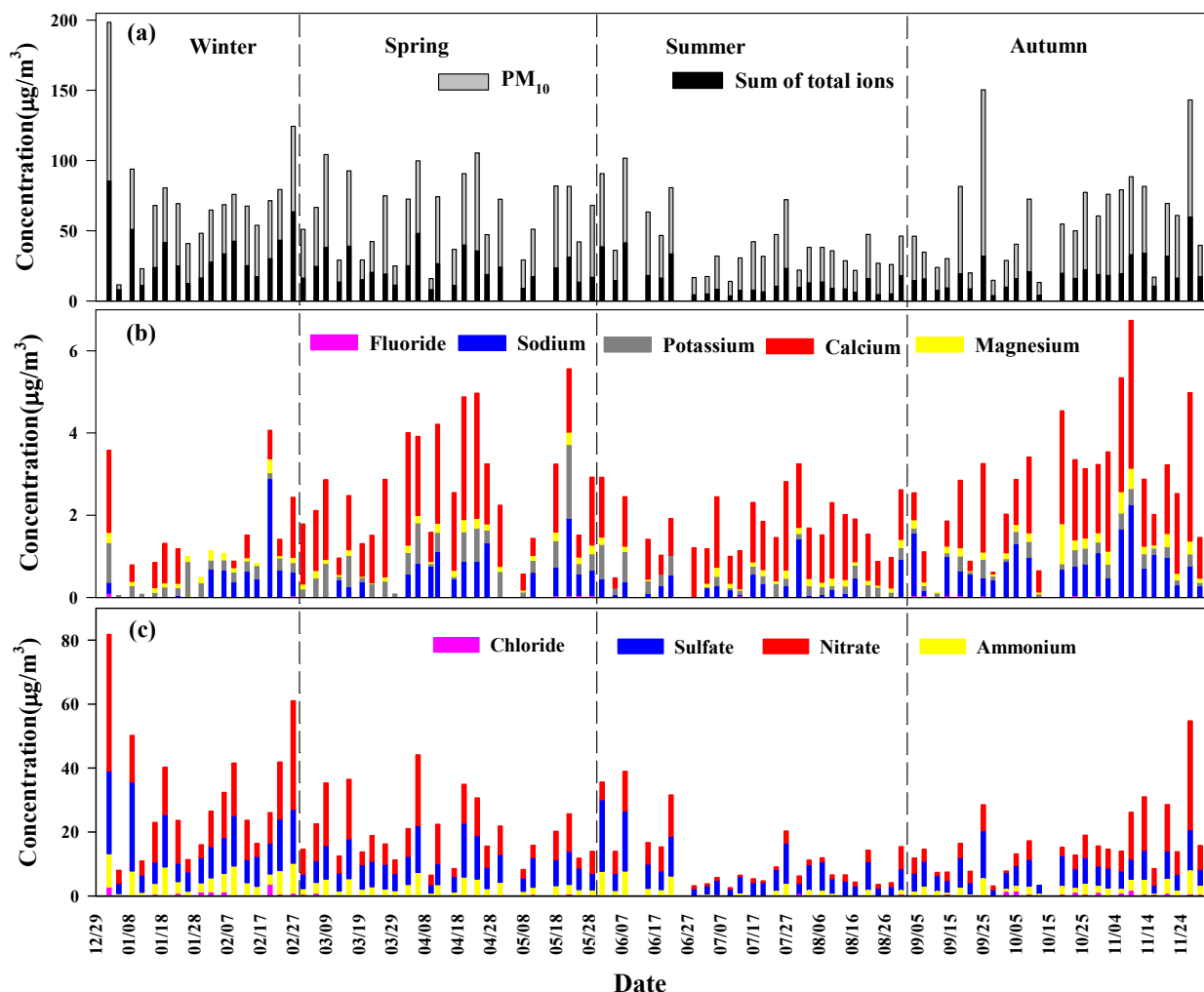


Fig. 1. Daily concentration of (a) PM_{10} and total ions; (b) F^- , Na^+ , K^+ , Ca^{2+} , Mg^{2+} ; (c) Cl^- , SO_4^{2-} , NO_3^- and NH_4^+ in 2017 at Lin'an Station.

3.2.3 $[\text{NO}_3^-]/[\text{SO}_4^{2-}]$

Generally, the ratio of $[\text{NO}_3^-]/[\text{SO}_4^{2-}]$ can be used as a tracer to characterize the relative importance of mobile and stationary sources in the atmosphere [7]. The high value of $[\text{NO}_3^-]/[\text{SO}_4^{2-}]$ showed the level of primary pollutants from the mobile sources was over the fixed sources. In our study, the annual mean ratio of $[\text{NO}_3^-]/[\text{SO}_4^{2-}]$ was 0.99 ± 0.65 , indicating that mobile sources and stationary sources were equally important in Lin'an. However, the ratio of $[\text{NO}_3^-]/[\text{SO}_4^{2-}]$ obtained in this study was lower than those in Shanghai(0.38-1.42), Beijing(1.16-1.31) and Nanjing(1.20-1.69) compared with other cities in China [18-20]. As shown in Fig. 2, the average ratios of $[\text{NO}_3^-]/[\text{SO}_4^{2-}]$ of PM_{10} in Lin'an station were 1.18 ± 0.56 , 1.06 ± 0.44 , 0.46 ± 0.36 and 1.02 ± 0.68 in winter, spring, summer and autumn,

respectively. The ratio (0.46 ± 0.36) observed in our study in summer was consistent with previous studies by Liang et al. (2017) at this station (the summer in 2015, 0.30 ± 0.17) in PM_{10} [20].

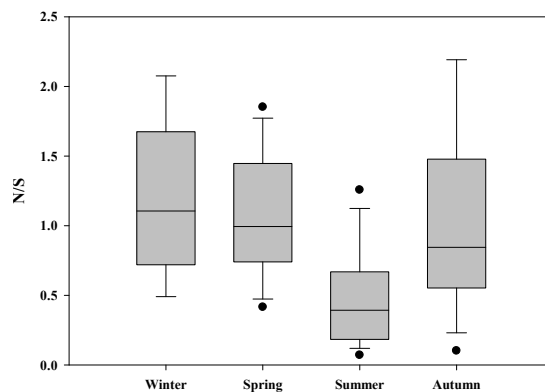
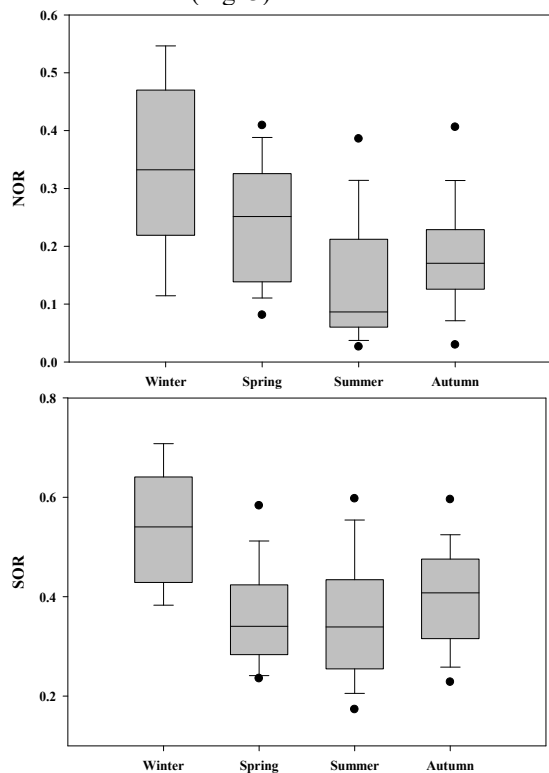


Fig.2. Seasonal variations of $[\text{NO}_3^-]/[\text{SO}_4^{2-}]$.

3.3 NOR and SOR

The secondary conversion was the major pattern for the formation of SNA and the levels of NO_3^- and SO_4^{2-} were strong related to atmospheric oxidation [4]. The nitrogen oxidation ratio (NOR) and sulfur oxidation ratio (SOR) were the indicators for the secondary formations. The NOR and SOR were calculated as following, $\text{NOR} = n\text{-NO}_3^- / (n\text{-NO}_3^- + n\text{-NO}_2)$ and $\text{SOR} = n\text{-SO}_4^{2-} / (n\text{-SO}_4^{2-} + n\text{-SO}_2)$. The annual mean NOR and SOR were 0.22 ± 0.13 and 0.41 ± 0.13 , respectively. As shown in Fig. 3, the average value of NOR was lowest in summer, which was mainly relevant to the formation mechanism of NO_3^- that was mostly existed with gaseous NO_3^- and not easily concentrated in particles with high temperature. Sachio et al. (1990) reported the value of SOR over 0.1 indicating sulfate was the production of SO_2 oxidized [21]. The seasonal mean values of SOR all exceeded 0.10, implying secondary formations was prominent in Lin'an (Fig. 3).

**Fig.3.** Seasonal variations of NOR and SOR.

4 Conclusions

The concentration of PM_{10} mass and nine water-soluble inorganic ions were performed in Lin'an to reveal their chemical characteristics and seasonal variations. The annual average PM_{10} concentration was $59.9 \pm 33.9 \mu\text{g m}^{-3}$, lower than those reported in previous studies, indicating air quality improvement in YRD region. Nine water-soluble inorganic ions was accounted for 30.2-45.1% of the total PM_{10} mass. The SNA were the major ions which contributed 86.3% to total ions.

The great difference among ions in four seasons was the concentration of NO_3^- which was lowest in summer while highest in winter, suggesting it was likely influenced by thermodynamics. The greater SO_4^{2-} was related to photochemical reaction and emissions of regional transportation. Except for the SNA, Ca^{2+} concentration was higher than other ions in every seasons due to sand storm and road fugitive dust. The annual mean ratio of $[\text{NO}_3^-]/[\text{SO}_4^{2-}]$ was 0.99 ± 0.65 , indicating mobile and stationary sources were equally important in Lin'an. The mean value of NOR and SOR were 0.22 ± 0.13 and 0.41 ± 0.13 , suggesting great NO_2 and SO_2 were oxidized to form $[\text{NO}_3^-]$ and $[\text{SO}_4^{2-}]$, respectively, in the atmosphere at the background station of YRD region.

Conflict of interest

The authors declare no conflict of interest.

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