Chemical Characteristics of Water-Soluble Ions in Particulate Matter in Three Metropolitan Areas in the North China Plain

Xu Dao¹, Zhen Wang²,³*, Yibing Lv¹, Enjiang Teng¹, Linlin Zhang¹, Chao Wang¹

¹. China National Environmental Monitoring Centre, Beijing, China, ². School of Resource and Environmental Sciences, Wuhan University, Wuhan, Hubei, China, ³. Department of Geography, University of California Santa Barbara, Santa Barbara, California, United States of America

* sinoo.whu@gmail.com

Abstract

PM₂.₅ and PM₁₀ samples were collected simultaneously in each season in Beijing, Tianjin and Shijiazhuang to identify the characteristics of water-soluble ion compositions in the North China Plain. The water-soluble ions displayed significant seasonal variation. The dominant ions were NO₃⁻, SO₄²⁻, NH₄⁺ and Cl⁻, accounting for more than 90% and 86% to the mass of total water-soluble ions in PM₂.₅ and PM₁₀, respectively. The anion/cation ratio indicated that the ion acidity of each city varied both between sites and seasonally. Over 50% of the ion species were enriched in small particles ≤1 μm in diameter. The [NO₃⁻]/[SO₄²⁻] ratio indicated that vehicles accounted for the majority of the particulate pollution in Beijing. Shijiazhuang, a city highly reliant on coal combustion, had a higher SO₄²⁻ concentration.

Introduction

Particulate matter (PM) in the atmosphere originates from either direct emission or physical and chemical transformation of gaseous pollutants [1–3]. Atmospheric aerosols have potential effects on human health, radiation balance, climate, and visibility [4, 5]. Air quality has become an increasing public health concern since a series of heavy pollutions of fine particulate matter (PM₂.₅, particles ≤2.5 μm in diameter) occurred in Beijing in 2011 winter. According to the WHO air quality guidelines and interim targets for particulate matter in developing countries, the 24–hour concentration of PM₁₀ and PM₂.₅ should be controlled below 150 and
75 µg/m³, respectively [6]. US EPA set the safe PM₁₀ and PM₂.₅ concentration at 50 and 35 µg/m³, respectively [7]. With the increase in public awareness of the degradation of visibility or hazy weather, China released the Chinese National Ambient Air Quality Standards (NAAQS) in 2012, taking 150 and 75 µg/m³ as the 24-hour PM₁₀ and PM₂.₅ limits in urban area, respectively, and 70 and 35 µg/m³ as the annual PM₁₀ and PM₂.₅ limits, respectively. Previous epidemiological research has shown that high levels of particulate pollution lead to increased morbidity and mortality, as well as respiratory symptoms [8–11]. Smaller particles are deposited more easily in the lungs [9], and are thus more harmful to health than larger particles [12]. The chemical composition of the particles is important for understanding atmospheric visibility [13], as well as the locations of deposition in the lung [14]. Water-soluble ions are a key area of atmospheric environmental research [15]. Water-soluble ions, such as NH₄⁺, Na⁺, K⁺, Ca²⁺, Mg²⁺, SO₄²⁻, NO₃⁻, F⁻ and Cl⁻, are significant components of atmospheric particles [16,17], which varies depending upon the particle source [18,19].

North China is one of the regions in China with the highest frequency of haze events [20,21]. According to the PM monitoring in Beijing during 2001 and 2003, the average 12-hour PM₁₀ mass concentration reached as high as 263.2 µg/m³ and PM₂.₅ ranged from 107 to 181 µg/m³ [22]. Another research showed the average PM₁₀ annual mass concentration were 124 µg/m³ in Beijing and 141 µg/m³ in Tianjin between 2009 to 2010 [23]. Both 24-hour and annual PM concentrations reported are far higher than the limits of NAAQS. Air pollution has increased as a function of population and the diversification of socio-economic activities. However, there have been few studies on PM₂.₅ and PM₁₀ with respect to their chemical composition and seasonal variation [24]. The majority of research on this region has focused on the composition [25], seasonal variation [26] and source of the particulate matter [27]. Generally, carbonaceous aerosol is the most abundant component of PM₂.₅ mass, and the main ions were NH₄⁺, SO₄²⁻ and NO₃⁻ [13,26,28]. Different dominant mechanisms for the formation of SO₄²⁻, NO₃⁻ and Cl⁻ are found in the summer and the spring [29]. Various aerosol speciations associated with PM pollution display a distinct seasonality [30]. Remote sources, which were primarily soil derived Ca²⁺, Mg²⁺ and Al, contribute a major part of the PM pollution in spring [13,30]. Seasonal peaks of organic carbon were commonly found in winter due to the high usage of coal for heating in the region [13,31]. Simulation showed that the PM₂.₅ concentration was sensitive to NH₃ emission [32]. In general, water-soluble ion species, including Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻, NO₃⁻, and SO₄²⁻, comprise 25%-50% of the aerosol mass predominantly in the form of sulfates, ammoniums and nitrates [33]. Water-soluble ions can scatter or absorb both incoming solar radiation and thermal radiation emitted from the Earth’s surface, thus directly change the radiation balance [34]. Previous studies mostly focused on a single size particle either in Beijing or in Tianjin [24,35]. Only a few studies addressed PM concentrations across the major cities in North China Plain [36]. In addition, these studies seldom referred to the national atmospheric background status at the same period. This study, derived from a national atmospheric monitoring
program in 2013, focuses on the water-soluble ion compositions and their variation in particulate matter in 3 metropolises in North China area. Also data from national atmospheric background sites are referred at the same sampling periods.

**Experiment**

1. **Sampling**

To compare the levels of the particulates and water-soluble ions in three cities (Beijing, Tianjin, Shijiazhuang) and four national atmospheric background sites, \(\text{PM}_{2.5}\) and \(\text{PM}_{10}\) samples were collected simultaneously at the seven sites in each season during 2013. Sampling locations of 3 studied cities were at the downtown area, while the background sampling sites were at remote rural area. Meanwhile samples from a control site at Datong city, which is close to the study area, were also collected. The field studies were carried out in the monitoring stations controlled or supervised by the China National Environmental Monitoring Centre (CNEMC). CNEMC has authority to permit our access to each station. Our field studies only collected atmospheric samples, which did not involve any endangered or protected species. The sampling sites are summarized in Table 1. Beijing, Tianjin and Shijiazhuang are located at the northwestern edge of the Great North China Plain, surrounded by mountains in all directions, except the south. The mountains extend several hundred kilometers and the highest peak is greater than 3000 m in elevation. The considerable emission of air pollutants in the region produces a high concentration of atmospheric particles.

A low-flow rate sampler, TH-16A (Tianhong, Wuhan, China) was deployed at the three city sites, and operated at a flow rate of 16.8 mL/min. A middle-flow rate sampler, TH-150 (Tianhong, Wuhan, China) was deployed at the four background sites, with a flow rate of 100 mL/min. Sampling was carried out at \(~\)23-h intervals, and conducted in each season for 5–7 days. The four periods were Feb 27th to Mar 10th in spring, Jun 19th to 30th in summer, Sep 10th to 29th in autumn, and Dec 7th to 29th in winter. Windy and/or rainy days were avoided collecting samples. 32 samples for National background point and 20–28 samples for each city site were sampled in each season. To assess the ion enrichment in particulate matter of various sizes, daily 23-h integrated PM\(_1\), PM\(_{2.5}\), PM\(_{10}\), TSP (from 10:00 am to 9:00 am the next day, local time) samples were collected with pure quartz fiber filters (MUNKTELL, Sweden) using a multi-stage sampler (Kalman, Hungary, Model KS-303.150.10/10/2.5/1+PAH7) in Beijing. Teflon filters (Pall International, Cat) were used to determine the concentrations by mass of the atmospheric particles, The filters were weighed with a microbalance before and after sampling under identical conditions in a temperature- and humidity-controlled room (20 ± 1°C and 35 ± 5% relative humidity).
2. Analysis

Each filter was transferred into a plastic jar with the particle collection side facing downwards, and then leached with 15-mL Milli-Q water (18.5 MΩ·cm⁻¹) in an ultrasonic bath for 30 min at room temperature. After ultrasonication, the leachate was filtered through a PTFE syringe filter (Fisher brand, 0.22 μm) before being introduced into an ion chromatography system (ICS-2000, Thermo Fisher). An AS19 analytical column (4 × 250 mm, Thermo Fisher), KOH eluent generator cartridge (EGC II KOH, Thermo Fisher) and 50-μL sample loop were employed for the determinations of anions, which included F⁻, Cl⁻, NO₃⁻, and SO₄²⁻. The cations of interest, Na⁺, NH₄⁺, K⁺, Ca²⁺, and Mg²⁺, were determined with the same IC system with a CS12A analytical column (4 × 250 mm, Thermo Fisher), a 50-μL sample loop and MSA (EGC II MSA, Thermo Fisher) as the eluent. The above-mentioned anions and cations were considered to be the total water-soluble ions in this study. The detection limit for major anions, including F⁻, Cl⁻, NO₃⁻, SO₄²⁻, Na⁺, NH₄⁺, K⁺, Ca²⁺, and Mg²⁺, was <2 μg/L. The recovery fell in the range 81–107%, and the precision based on seven duplicate spike samples was 3%.

All obtained data were categorized according to where and which season they were collected. Further statistical analysis including mean/variance, Pearson correlation and linear fits were calculated in the statistical package of Matlab 2013b software. Then, ion balance was used to evaluate the acid-base balance of the aerosol particles. We converted the ion concentration by mass into micro-equivalents, as follows:
C(cation micro – equivalents m⁻³) = \( \frac{\text{Na}^+}{23} + \frac{\text{NH}_4^+}{18} + \frac{\text{K}^+}{39} + \frac{\text{Mg}^{2+}}{12} + \frac{\text{Ca}^{2+}}{20} \) (1)

A(anion micro – equivalents m⁻³) = \( \frac{\text{F}^-}{19} + \frac{\text{Cl}^-}{35.5} + \frac{\text{NO}_3^-}{62} + \frac{\text{SO}_4^{2-}}{48} \) (2)

Micro-equivalents were also used for linear fits of secondary ions in Matlab 2013b software system.

Results and Discussion

1. Seasonal variation of total water-soluble ions

Significant seasonal variation in the water-soluble compositions of PM₂.5 and PM₁₀ were identified in each city (Table 2). In spring, autumn and winter, the ions exhibited a similar concentration distribution, with the exception of a minor difference in SO₄²⁻ in PM₂.5 during spring. The order of the total ion concentrations in the three cities was Shijiazhuang > Tianjin > Beijing. The SO₄²⁻ concentration in spring in the PM₂.5 of Tianjin was slightly higher than that of Shijiazhuang. However, an inverse distribution was found in the summer. The ion concentrations of Shijiazhuang were lower than those of Beijing and Tianjin. During the sampling period, the average PM₂.5 and PM₁₀ concentrations by mass of the whole studied region were 167 and 273 \( \mu \text{g/m}^3 \), respectively. The concentrations of water-soluble ions in both PM₂.5 and PM₁₀ displayed a significant variation with season, in the order spring > winter > summer > autumn. This might be explained by the high proportion of coal burning for heating in spring and winter, and the frequent dust storms in spring [39].

2. Ionic species

The proportions of each water-soluble ion also presented a clear pattern. The concentrations of the ions were: NO₃⁻ > SO₄²⁻ > NH₄⁺ > Cl⁻ > Ca²⁺ > K⁺ > Na⁺ > F⁻ > Mg²⁺ in spring and autumn; SO₄²⁻ > NO₃⁻ > NH₄⁺ > Cl⁻ > Na⁺ > Ca²⁺ > K⁺ > Mg²⁺ > F⁻ in summer; and SO₄²⁻ > NO₃⁻ > NH₄⁺ > Cl⁻ > K⁺ > Ca²⁺ > Na⁺ > F⁻ > Mg²⁺ in winter. In PM₂.5, the concentrations of NO₃⁻, SO₄²⁻, NH₄⁺ and Cl⁻ were significantly higher than those of the remaining five ions, comprising 90.3–92.3% of the total mass of water-soluble ions in each season. The total concentrations of these four dominant ions exceeded 70 \( \mu \text{g/m}^3 \) in all samples. PM₁₀ had similar ion species characteristics to PM₂.5. Four dominant ions contributed 86.1%–88.6% of the total mass of water-soluble ions in each season, ranging from 37–195 \( \mu \text{g/m}^3 \). The concentrations of Ca²⁺, K⁺ and Na⁺ were
comparatively low, with average concentrations of 2.90, 2.27 and 1.82 μg/m³, respectively in PM$_{2.5}$ and slightly higher average concentrations in PM$_{10}$. Mg$^{2+}$ and F$^-$ combined contributed less than 0.5% of the total mass of ionic species.
The concentration of $F^-$ at the Shijiazhuang site ranged from 0.014–2.436 $\mu$g/m$^3$ in PM$_{2.5}$ and from 0.046–3.473 $\mu$g/m$^3$ in PM$_{10}$, an average concentration more than threefold greater than those at Beijing and Tianjin.

Differences in the dominant ions were found between the study area and the background sites. The $NO_3^-$ concentration was similar to or even greater than the $SO_4^{2-}$ in the study area, compared higher concentration of $SO_4^{2-}$ than $NO_3^-$ at the background sites. $Cl^-$ and $Ca^{2+}$ concentrations were one order of magnitude greater than those of $K^+$ and $Na^+$, while they were similar at the background sites. To give a broader picture, ion concentrations in PM$_{2.5}$ of other important city in eastern Asian were shown in Table 3. The concentrations of $NO_3^-$ and $SO_4^{2-}$ were similar between Beijing and Shanghai, while $NO_3^-$ concentrations were higher in Beijing than in Guangzhou. $SO_4^{2-}$ concentrations were similar between the two cities. The three eastern Asia cities outside China had smaller equivalent ion concentrations.

The Datong site was used as the control point. It is located in the upwind direction of the study area, and is isolated by the Taihang Mountains. Here too, the dominant ions were $NO_3^-$, $SO_4^{2-}$, $NH_4^+$, and $Cl^-$. However, the concentrations were lower than those of the study area (Figure 1). The concentration of $SO_4^{2-}$ in spring was highest in Datong, 11.69 $\mu$g/m$^3$ in PM$_{10}$. The average concentration of $SO_4^{2-}$ in the study area reached 39.26 $\mu$g/m$^3$, almost 3.4-fold greater than in Datong. The concentrations of the remaining ions in each sample were less than 10 $\mu$g/m$^3$, significantly lower than in the study area.

Ion concentrations of study cities were divided by corresponding average ion concentration of 4 background sites. Namely, concentration multiples of study cities to background sites were used to calculate Pearson correlation coefficient for each site (Table 4). The water-soluble ion concentrations in PM$_{2.5}$ were similar in the 3 case study cities (correlation coefficient $>0.8334$, $p<0.05$) and displayed relatively low similarity between 3 case study cities and Datong. This implied that the North China sites might have similar sources of PM$_{2.5}$. There was a significant correlation between Datong and Shijiazhuang, and between Beijing and Tianjin in PM$_{10}$ (correlation coefficient $>0.8047$, $p<0.05$). This implies that fugitive dust contributed a larger share of particles to Shijiazhuang. This is supported by the significantly higher $Ca^{2+}$ concentration in Shijiazhuang, which is derived primarily from soil sources.

Correlations between the anion and cation equivalents were observed (Figure 2). Ion balance calculations stratified by season showed that summer and autumn samples were above the A/C (anion/cation) unity line in both PM$_{2.5}$ and PM$_{10}$, indicating that anion was excessive. In contrast, the spring anion was insufficient; i.e., below the A/C unity line. In winter, the ion balance relationships were inconsistent between PM$_{10}$ samples and PM$_{2.5}$ samples, indicating that the sources of PM$_{10}$ and PM$_{2.5}$ were different in winter. Higher regression slopes were found in PM$_{2.5}$ samples. The reason might be the precursors of $SO_4^{2-}$ and NO$_x$, which enriched primarily in the small particulate matter. A steeper slope was observed in summer primarily because SO$_2$ and NO$_x$ were more easily oxidized to H$_2$SO$_4$ and HNO$_3$ and accumulated in the aerosols under the intensive
illumination and high temperature [45]. A/C also varied by size and site location. Annual A/C ratios of PM$_{2.5}$ in Beijing and in Shijiazhuang were smaller than 0.9, but larger than 1.1 in Tianjin. When coming to the PM$_{10}$, Beijing and Tianjin were very close to 1.0. These results demonstrate that anions tend to be distributed in small particles.

3. Ion enrichment in particulate matter of various sizes

The size of the particulate matter affected its capability for ionic enrichment. The total mass concentration of the dominant ions contained in PM$_{2.5}$ was about 60%-90% of the mass concentration of the dominant ions contained in PM$_{10}$ (See

| Ions | Beijing n=96 | Tianjin n=80 | Shijiazhuang n=96 | Datong n=104 | Guangzhou, China [46] | Shanghai, China [47] | Singapore [48] | Yokohama, Japan [49] | Seoul, South Korea, [50] |
|------|--------------|--------------|-------------------|--------------|------------------------|---------------------|---------------|-----------------------|-------------------------|
| F$^-$ | 0.24         | 0.18         | 0.91              | 0.13         | –                      | –                   | –             | –                     | –                       |
| Cl$^-$ | 5.88         | 7.38         | 13.84             | 1.58         | 1.8                    | 2.34                | 0.6           | 0.21                  | 0.17                    |
| NO$_3$ | 25.06        | 29.1         | 36.75             | 3.31         | 7.8                    | 22.2                | 0.9           | 1.9                   | 5.17                    |
| SO$_4^{2-}$ | 17.08       | 29.64        | 31.89             | 6.26         | 18.1                   | 26.7                | 5.0           | 4.9                   | 5.77                    |
| Na$^+$ | 1.34         | 1.61         | 3.27              | 0.45         | 2.2                    | 0.53                | 0.6           | 0.68                  | 0.12                    |
| NH$_4^+$ | 11.95        | 15.78        | 22.54             | 2.82         | 5.1                    | 4.54                | 1.62          | 1.10                  | 3.70                    |
| K$^+$ | 1.7          | 2.33         | 3.59              | 0.68         | 0.9                    | 0.27                | 0.53          | 0.16                  | 0.33                    |
| Mg$^{2+}$ | 0.17         | 0.24         | 0.68              | 0.13         | –                      | 0.20                | 0.07          | 0.12                  | 0.04                    |
| Ca$^{2+}$ | 2.58         | 1.83         | 7.79              | 1.21         | 0.4                    | 1.56                | 0.29          | 0.76                  | 0.14                    |

Figure 1. Seasonal variation of water-soluble ions in the study area and at the control point.

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Figure 1. Seasonal variation of water-soluble ions in the study area and at the control point.
Table 4. Pearson correlation among study sites and control site by using seasonal average concentration multiples of study cities to background sites.

|        | Beijing | Tianjin | Shijiazhuang | Datong |
|--------|---------|---------|--------------|--------|
| Beijing| 0.8047  | 0.3387  | 0.2770       |        |
| Tianjin| 0.9594  | 0.5003  | 0.4566       |        |
| Shijiazhuang| 0.8333  | 0.8334  | 0.9120       |        |
| Datong | 0.4783  | 0.4977  | 0.6758       |        |

(The bold numbers were calculated based on PM$_{10}$, and the regular numbers were based on PM$_{2.5}$). (4 seasons, 9 ions, n=36, p<0.05).

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Table 2). That is, more ions were distributed in the fine particle (PM$_{2.5}$) than in the coarse particle (PM$_{2.5}$–PM$_{10}$). The enrichment of non-dominant ions displayed more complex relationships. In spring and summer, ~50 –80% of F$^-$ was found in PM$_{2.5}$ at each site, while in autumn and winter the proportion dropped to 17–37%. The Na$^+$ and K$^+$ distributions were similar to those of the dominant ions, with an annual range of 59–96%, with the exception of Na$^+$, which was present at a concentration of 43% in summer in Beijing. Greater complexity was displayed by the Ca$^{2+}$ and Mg$^{2+}$ distributions, both seasonally and spatially. <30% Ca$^{2+}$ and <50% Mg$^{2+}$ were found in PM$_{2.5}$ in Beijing. That is, the source of Ca$^{2+}$ and Mg$^{2+}$ in Beijing was primarily large particles. High proportions of Ca$^{2+}$ and Mg$^{2+}$ in PM$_{2.5}$ in spring and summer (~49 –90%), and low proportions in autumn and winter (<25%) were found in Tianjin. The proportion of Ca$^{2+}$ in PM$_{2.5}$ in Shijiazhuang decreased from 55% in spring to 25% in winter. The proportion of Mg$^{2+}$ in PM$_{2.5}$ peaked in summer at ~70%, and...
decreased to 23% in winter. Hence, the source of non-dominant ions might vary from site to site.

To investigate the ion enrichment of the different sizes of particulate matter, a further study was conducted in Beijing. We collected and analyzed PM$_1$, PM$_{2.5}$, PM$_{10}$ and total suspended particulate matters (TSP). Figure 3 shows the concentrations of nine ions in particulate matter of different sizes. The smaller diameter particulate matter contained the highest concentration of soluble ions. For example, >56% of the water-soluble ions were distributed in PM$_1$, compared to <10% in particles with a diameter >10 μm. Small particulate matter was more capable of carrying K$^+$. While Cl$^-$, Mg$^{2+}$, and Ca$^{2+}$ were present at higher concentrations in the larger sizes of particulate matter. Thus, controlling small particulate matter would substantially reduce the concentration of water-soluble ions in the atmosphere.

4. Secondary ions

Secondary ions play a key role in the formation of particulate matter [46–48]. The non-organic secondary ions NH$_4^+$, SO$_4^{2-}$ and NO$_3^-$ accumulate under stable weather conditions. Secondary ions also affect atmospheric visibility and human health [49]. The total mass of secondary ions contributed 42.4% and 31.5% of the PM$_{2.5}$ and PM$_{10}$, respectively. The major water-soluble ions were the secondary inorganic ions sulfate, nitrate and ammonium, which accounted for 77% of the total water-soluble ions in Beijing in 2008 [50]. The ratio of [NO$_3^-$]/[SO$_4^{2-}$] in aerosols can be used to analyze the contribution of mobile sources (such as vehicle exhaust) to stationary sources (such as boilers) [51]. Coal is the main source of

Figure 3. Ion enrichment in particulate matter of different sizes.

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SO2 emissions. NOx originates from motor vehicles and coal burning [52, 53]. An increased NO3⁻ contribution to PM1 mass loading during polluted periods has been reported [54]. Table 5 shows the [NO3⁻]/[SO4²⁻] ratios of the different sites and seasons. The ratios during summer were smaller than those in the other three seasons because the high temperatures transform particulate nitrate into the gaseous state, thus reducing the [NO3⁻]/[SO4²⁻] ratio [55]. In winter, the [NO3⁻] < [SO4²⁻] in Tianjin and Shijiazhuang implies a dominance of sulfate pollution from heating and industrial coal burning. In contrast, in Beijing, [NO3⁻] > [SO4²⁻] and the concentration of NOx continued to increase in Beijing in 2011 [56], which indicates that vehicles made a greater contribution to emissions than in Tianjin and Shijiazhuang.

The differences among the three cities reflect both the dramatic increase in vehicle numbers and the decreased usage of coal at the different stages of urban development (Table 6). Beijing had the largest contribution from vehicles, which was threefold greater than that of Shijiazhuang. Vehicles have already become one of the main contributors to particle emissions in metropolitans as the one of the main source of NO3⁻ [57]. For example, direct emission, road dust and secondary nitrates, which were closely related to vehicle use, contributed 27.9%-47.5% to total PM2.5 mass concentration in Beijing [37]. Larger transportation sector in Beijing and Tianjin consumed more petroleum, thus contributed more NO3⁻ emission. The industrial structure of the cities, which we did not investigate in depth, was the cause of the difference between coal and petroleum consumption. Coal was the main energy source, combustion of which results in release of both NO3⁻ and SO4²⁻. Shijiazhuang relied substantially on coal combustion, at a level almost threefold greater than that in Beijing. High coal combustion produces higher SO2 emissions, leading to higher SO4²⁻ concentrations. Therefore [NO3⁻]/[SO4²⁻] ratio here was close related to the energy use in the transport sector and the industrial sector.

Secondary ions have complex reactions. NH4⁺ readily reacts with SO4²⁻ to the stable form of ammonium salts [50, 61, 62]. The reaction of NH4⁺ and NO3⁻ is affected by the gas/aerosol distribution of the precursor gases (NH3 and HNO3) in terms of temperature and humidity [63]. [NH4⁺] was linearly correlated with the micro-equivalent sum of ([SO4²⁻]+[NO3⁻]) in the three cities. The linear fits of the data were:

| NO3⁻/SO4²⁻ | Beijing PM2.5 | Beijing PM10 | Tianjin PM2.5 | Tianjin PM10 | Shijiazhuang PM2.5 | Shijiazhuang PM10 |
|------------|--------------|--------------|---------------|--------------|--------------------|------------------|
| Spring     | 2.36         | 2.07         | 1.35          | 1.24         | 1.86               | 1.56             |
| Summer     | 0.83         | 0.97         | 0.71          | 0.86         | 0.56               | 0.62             |
| Autumn     | 1.12         | 1.35         | 1.13          | 1.39         | 1.04               | 0.87             |
| Winter     | 1.47         | 1.40         | 0.81          | 0.80         | 0.92               | 0.98             |

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The PM$_{2.5}$ regression slopes were $<$1 in Beijing and Tianjin, but slightly $>$1 in Shijiazhuang. The PM$_{10}$ regression slopes of [NH$_4^+$] against ([SO$_4^{2-}$]+[NO$_3^-$]) at the three cities were $<$1, indicating that SO$_4^{2-}$ and NO$_3^-$ in large particles were incompletely neutralized. Larger slope coefficients and higher NH$_4^+$ concentrations were found in Shijiazhuang. One possible reason for this was the greater agricultural fertilizer usage (489.0 million tons in Shijiazhuang, compared to 136.7 million tons in Beijing and 244.5 million tons in Tianjin in 2012. Data from 2013 were not available at the time of our study), which was one of the primary sources of NH$_4^+$. Since evaporated ammonium was not taken into account, the extent of SO$_4^{2-}$ and NO$_3^-$ neutralization might have been underestimated.
Conclusion

The concentration gradient of total water-soluble ions was in the order Shijiazhuang > Tianjin > Beijing. Spring had the highest concentrations. The total concentrations by mass for summer and winter were similar, and higher than those in autumn. The gradient of ion species across the North China region was $\text{NO}_3^-$, $\text{SO}_4^{2-}$ > $\text{NH}_4^+$ > $\text{Cl}^-$ > $\text{Ca}^{2+}$, $\text{K}^+$, $\text{Na}^+$ > $\text{Mg}^{2+}$, $\text{F}^-$. $\text{NO}_3^-$, $\text{SO}_4^{2-}$, $\text{NH}_4^+$, and $\text{Cl}^-$ were the dominant ion species, contributing more than 90% and 86% of the concentration by mass of the total water-soluble ions in PM$_{2.5}$ and PM$_{10}$, respectively. The size of the particulate matter was an important determinant of the ion composition. Over 50% of the water-soluble ions were present in PM$_1$, and 73.9%-94.9% in PM$_{2.5}$. Secondary ions, including $\text{NO}_3^-$, $\text{SO}_4^{2-}$ and $\text{NH}_4^+$, comprised 43.4% and 31.5% of the total average concentrations by mass. The $[\text{NO}_3^-]/[\text{SO}_4^{2-}]$ ratio indicated that the contribution of vehicle pollution increased with economic development. The anion/cation balance varied among sites and seasons, indicating that the source might be complex. The balance of secondary ions was likely influenced by the usage of agricultural fertilizer. The pollution patterns of the whole area were somewhat significantly correlated. Further studies of organic carbon and pollution source apportionment are needed.

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Author Contributions

Conceived and designed the experiments: XD YL ET LZ CW ZW. Performed the experiments: XD. Analyzed the data: ZW XD. Contributed reagents/materials/analysis tools: XD YL ET LZ CW. Wrote the paper: ZW XD.

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