Analysis of Characteristics of Soluble Ion Pollution in Atmospheric PM2.5 in Shenyang City

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Abstract: The concentration characteristics of water-soluble ions in atmospheric fine particulate matter PM2.5 in Shenyang City were studied. Correlation analysis was carried out on the tested components. The results showed that SO₄²⁻ and NO₃⁻ in the water-soluble ion concentration of PM2.5 in Shenyang City. The three ions of NH₄⁺ account for a higher total ion concentration, accounting for 35.2%, 34.7%, and 11.6%, respectively. It was found that due to the unique terrain and climate of Shenyang, the spring pollution was more serious. Correlation analysis showed that the main forms of water-soluble ions in PM2.5 in Shenyang City were NO₃NH₄, KNO₃, MgSO₄, CaSO₄ and so on.

1. Introduction

In recent years, China’s air pollution problem has become serious. Previous studies have shown that even low concentrations of air pollution are harmful to the health of residents and even cause some diseases. The World Health Organization (WHO) has estimated[1] that air pollution can cause 800,000 deaths per year worldwide and 4.6 million people's life expectancy is reduced. Substances in PM2.5, especially NOx, SO2, O₃, cause great damage to the human health. Studies have shown that NOx and SO2 can damage the lungs and heart, which can lead to lung or heart disease and even death. Foreign studies have found that soluble ions of atmospheric particulate matter also cause cardiovascular disease[4]. SO₄²⁻, K⁺, Ca²⁺, and NO₃⁻ have the most significant effects on human health, especially SO₄²⁻, NO₃⁻, which are mainly derived from gas precursors. The conversion is therefore also referred to as a secondary inorganic aerosol.

Shenyang is located in the geographical center of Northeast Asia, with the hilly mountains of Liaodong in the east and the hills of northern Liaoning in the north. The terrain gradually flattens west and south. Shenyang is the capital of Liaoning Province. It used to be an industrial city. Although the proportion of industrial production in Shenyang is decreasing, the air pollution in winter is still dominated by coal combustion. In the spring, summer and autumn, the dust source contributed a lot to PM2.5, and now the motor vehicle source accounts for the main contribution. In this study, PM2.5, a fine particulate matter in Shenyang, was sampled. From April 2018 to January 2019, 40 samples were collected. The samples were obtained by ion chromatography to obtain the concentration of seven ions, including Na⁺, Mg²⁺, K⁺, Ca²⁺, NH₄⁺, SO₄²⁻, NO₃⁻.
2. Materials and methods

2.1 Sampling location and sampling method
PM2.5 samples were collected in different positions, as shown in Table 1.

| Sampling site          | Northeastern University | Wu ai market | Olympic Sports | Shun xin Community | Shenyang University | Liaoning University |
|------------------------|-------------------------|--------------|----------------|---------------------|---------------------|---------------------|
| Number of samples      | 10                      | 8            | 7              | 6                   | 6                   | 9                   |

The sampling device is placed 2 to 3 meters above the ground. Sample collection was performed according to HJ 656-2013.

Consider the filter background problem used for sampling. Twenty-three-hour PM2.5 samples collected on quartz filters produced by Whatman. The sample was collected by the 2030 TSP sampling device, which produced by Qingdao Laoying, and the flow was 100 L/min. In addition, wear nitrile gloves during the sampling process, and put the numbered and weighed filter into the clean filter holder with the non-serrated tweezers. The matte side of the filter should face the intake direction. Firmly compress the filter.

2.2 Sample storage and analysis
After the sample was weighed, the collected particles of the filter were folded inwardly twice, placed in a ziplock bag and stored in a refrigerator at -4 °C, and all the analysis was completed within 3 months. Before the sample analysis, the filter was cut into small pieces and placed in a 20 ml glass bottle. After adding 15 ml of deionized water, ultrasonic extraction was carried out for 10 min. The supernatant was taken to volume, then samples were analyzed by ICS-5000+ ion chromatograph.

3. Results and discussion

3.1 Analysis of water-soluble ion concentration
The maximum, minimum and average values of various ion concentrations during the sampling period are shown in Table 2.

| Ion | NO$_3^-$ | SO$_4^{2-}$ | NH$_4^+$ | K$^+$ | Mg$^{2+}$ | Na$^+$ | Ca$^{2+}$ |
|-----|----------|-------------|----------|-------|-----------|-------|-----------|
| max | 20.301   | 14.370      | 4.107    | 1.574 | 1.229     | 1.528 | 3.801     |
| min | 0.496    | 1.832       | 0.006    | 0.006 | 0.001     | 0.383 | 0.038     |
| avg | 6.322    | 6.233       | 2.099    | 0.678 | 0.275     | 0.740 | 1.609     |

It can be seen from Table 2 that the various ion concentrations are ranked from high to low: NO$_3^-$>SO$_4^{2-}$>NH$_4^+$>Ca$^{2+}$>Na$^+$>K$^+$>Mg$^{2+}$, among which SO$_4^{2-}$, NO$_3^-$, NH$_4^+$ ions account for the highest total ion concentration, accounting for 35.2%, 34.7%, and 11.6%, respectively. The sum of the three is 81.5%, which is consistent with previous studies.

3.2 Seasonal change of soluble ions
Due to changes in meteorological factors and other conditions, the total concentration of water-soluble ions and the concentration of various ions in different seasons also change. It can be found from Figure 2 that SO$_4^{2-}$, NO$_3^-$, and NH$_4^+$ account for a large proportion in different seasons. The main components of water-soluble ions in Shenyang City, the road repair in Shenyang in the spring and autumn, community transformation, and the large wind and sand in Shenyang in the spring and autumn seasons, Ca$^{2+}$ and Mg$^{2+}$ in spring and summer accounted for higher in autumn and winter. In contrast, the total concentration of water-soluble ions is the highest in spring, which is presumably because the heating period in Shenyang is longer, and the temperature difference between day and night in Shenyang is large at the beginning of spring, and the maximum temperature difference can
reach 15 °C, which easily leads to the formation of inversion temperature, leading to accumulation of pollutants.

![Fig1 Concentration of ions in different seasons](image)

**Fig1 Concentration of ions in different seasons**

### 3.3 Soluble ion correlation analysis

In order to understand the relationship between water-soluble ions and to preliminarily speculate on their source and presence, SPSS software was used to analyze the correlation of ions. Generally speaking, when the correlation coefficient \( r \) is between 0.8 and 1, the correlation is extremely strong; between 0.6 and 0.8 indicates strong correlation; between 0.4 and 0.6 indicates moderate correlation; between 0.2 and 0.4 indicates weak correlation; 0 to 0.2 It is said that the correlation is extremely poor. It can be seen from the table that the correlation coefficient of NO\(_3^-\) and NH\(_4^+\) is above 0.8, indicating that NO\(_3^-\) and NH\(_4^+\) are significantly correlated, and the correlation between NO\(_3^-\) and K\(^+\) is also significant. Therefore, NO\(_3^-\) and NH\(_4^+\) of PM2.5 are more combined into NO\(_3^-\)NH\(_4^+\). There are also some NO\(_3^-\) that may generate KNO\(_3\). SO\(_4^{2-}\) has strong correlation with Mg\(^{2+}\) and Ca\(^{2+}\), indicating that SO\(_4^{2-}\) in PM2.5 may generate more MgSO\(_4\) and CaSO\(_4\). In addition, NH\(_4^+\) has higher correlation with K\(^+\), and Ca\(^{2+}\) and Mg\(^{2+}\) are also the same. K\(^+\) can be used as a marker of biomass combustion. Therefore, the high correlation coefficient of the former indicates that NH\(_4^+\) may be more derived from biomass burning, waste incineration and the like. Both Ca\(^{2+}\) and Mg\(^{2+}\) are the marking materials for building dust sources. Due to the increase of construction, the correlation between the two ions is enhanced, and the contribution of building sources to PM2.5 may be greater. In summary, the main forms of water-soluble ions in PM2.5 of Shenyang City are NO\(_3^-\)NH\(_4^+\), KNO\(_3\), MgSO\(_4\), CaSO\(_4\) and so on.

**Table 3 Correlation coefficient of each ion**

|        | NO\(_3^-\) | SO\(_4^{2-}\) | NH\(_4^+\) | K\(^+\) | Mg\(^{2+}\) | Na\(^+\) | Ca\(^{2+}\) |
|--------|------------|--------------|------------|--------|-------------|---------|------------|
| NO\(_3^-\) | **1**      |              |            |        |             |         |            |
| SO\(_4^{2-}\)| **0.590** | **1**        |            |        |             |         |             |
| NH\(_4^+\)| **0.823** | **0.560**   | **1**      |        |             |         |             |
| K\(^+\)| **0.656** | **0.446**   | **0.722** | **1**  |             |         |             |
| Mg\(^{2+}\)| **0.404** | **0.621**   | **0.231** | **0.418** | **1** |         |             |
| Na\(^+\)| **0.406** | **0.585**   | **0.044** | **0.283** | **0.482** | **1** |             |
| Ca\(^{2+}\)| **0.554** | **0.736** | **0.333** | **0.534** | **0.730** | **0.594** | **1** |

** indicates a confidence level of \(p<0.01\), and the correlation is significant; * indicates a confidence level of \(p<0.05\), and the correlation is significant.
4. conclusion
1) The concentration of water-soluble ions in PM2.5 of Shenyang City is as follows: \( \text{NO}_3^- > \text{SO}_4^{2-} > \text{NH}_4^+ > \text{Ca}^{2+} > \text{Na}^- > \text{K}^- > \text{Mg}^{2+} \), among which the three ions of \( \text{SO}_4^{2-}, \text{NO}_3^- \) and \( \text{NH}_4^+ \) account for the highest total ion concentration, accounting for 35.2%, 34.7%, and 11.6% respectively. The main components of inorganic water-soluble ions in Shenyang. In addition, due to the long heating period and the special temperature difference in the Shenyang area, the water-soluble ion concentration in the early spring season is relatively high, and smog frequently occurs.

2) The main forms of water-soluble ions in PM2.5 in Shenyang City are \( \text{NO}_3^-\text{NH}_4^+ \), \( \text{KNO}_3 \), \( \text{MgSO}_4 \), \( \text{CaSO}_4 \), etc. The correlation between \( \text{Ca}^{2+} \) and \( \text{Mg}^{2+} \) is enhanced, indicating that the contribution of building source to PM2.5 may be large.

Acknowledgment
This work has been financially supported by the Science and Technology Project of Shenyang (17-178-9-00)

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