Construction of Fine Particles Source Spectrum Bank in Typical Region and Empirical Research of Matching Diagnosis

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Abstract. The research object of this paper is fine particles in typical region. The construction of component spectrum bank is based on the technology of online source apportionment, then the result of the apportionment is utilized to verify the effectiveness of fine particles component spectrum bank and which also act as the matching basis of online source apportionment receptor sample. On the next, the particle source of air pollution is carried through the matching diagnosis empirical research by utilizing online source apportionment technology, to provide technical support for the cause analysis and treatment of heavy pollution weather.

1. Introduction
As social economic developing rapid, the fine particles gradually become a key factor which affects the ambient air quality especially in heavy pollution periods. Moreover, the fine particles are a significant cause of low atmospheric visibility [1-3]. Beijing-Tianjin-Hebei region is a high-prevalence area of heavy air pollution its compound atmospheric pollution features is different from the other regions of China. Taking Tianjin as the typical region of this research and utilizing SPAMS to analyze the changes of fine particles component during heavy pollution period, thereby to provide technical support for the cause analysis of heavy pollution weather [4, 5].

2. Construction of Fine Particles Component Spectrum Bank

2.1. Sampling
The sampling selection is based on source apportionment result that released by Tianjin and we finally selected five categories of source pollution, respectively are raise dust, coal combustion, motor vehicle, biomass burning and catering which have larger contribution to the local pollution. The author adopted SPAMS to carry out the apportionment and obtained the online source apportionment component spectrum of fine particles in Tianjin, and which also act as the matching basis of pollutant features in heavy pollution weather. As regards the road dust, soil dust and construction cement dust, the collected sample need to be dried in the air and maintain its original state without grinding. Employing 150-mesh sieve to griddle the dust and taking the minus sieve dust and then connect to the equipment to analyze through electrically conductive silicone pipe by means of resuspension and adopt air bag or
vacuum flask to collect the dust samples, without carrying out any treatment and directly connect to the equipment through electrically conductive silicone pipe and conduct analysis. If the humidity of the sample gas is large then it should connect to the drying pipe first while sample injection and enter into the equipment to carry out analysis after getting through the drying pipe[6, 7].

2.2. Data Analysis
The analytical instrument we adopted is SPAMS. The ambient air sample are cut by the PM$_{2.5}$ cutting head first and then enter into the SPAMS through sample injection micro pore. The fine particles of the air would go through the aerodynamic lens, laser diameter measuring instrument, ionization laser and mass analyzer to realize the detection of aerosol particle chemical constituents. The data analysis method we adopted is YAADA single particle mass spectrometric data analysis software based on Matlab platform and the core of it is self-adaption resonance theory neural network classification algorithm(ART-2a)which could proceed intelligent classification for a myriad of data. The relevant parameters of this algorithm in this paper are set as following: vigilance factor 0.85, learning efficiency 0.05, and iterations 20. After analysis, the particles of each category would be classified into hundreds categories and then artificially merge these categories according to the features of ionic composition and finally obtain the fine particles source composition spectrum bank of Tianjin.

2.3. Characteristic Spectrum of Fine Particles Composition

![Figure 1 Characteristics of dust source](image1)

![Figure 2 Characteristics of coal combustion source](image2)

![Figure 3 Characteristics of motor vehicle source](image3)

![Figure 4 Characteristics of biomass burning sources](image4)
The characteristic elements of the raise dust source (Figure 1) in the positive spectrogram are Mg\(^+\), Al\(^+\), Si, Ca\(^+\) and its oxide, Cu\(^+\), Pb and a small amount of organic carbon; the negative spectrogram include NO\(_2\)\(^-\), NO\(_3\)\(^-\), HSO\(_4\)\(^-\), PO\(_2\)\(^-\), PO\(_3\)\(^-\), SiO\(_3\)\(^-\), C\(_2\)\(^-\), CN\(^-\), CNO\(^-\), Cl\(^-\), \(\text{OH}^+\), K\(^+\), Pb\(^+\), Fe\(^+\), etc. After comparison, we find that the typical compositions of the coal combustion source are Fe\(^+\) and Pb\(^+\) and the negative spectrogram may appear the element carbon and organic carbon.

The positive spectrogram of the motor vehicle source (Figure 3) include element carbon, Ca\(^+\), Mn\(^+\) and long-chain element carbon HEC and the negative spectrogram of the motor vehicle source include the characteristic peaks of NO\(_2\)\(^-\), NO\(_3\)\(^-\), EC and HSO\(_4\)\(^-\).

The positive spectrogram of the biomass burning source (Figure 4) with strong K\(^+\) signal peak and its cluster K\(_2\)Cl\(^+\), K\(_2\)O\(_2\)\(^+\), characteristic peaks and organic carbon characteristic peak; the negative spectrogram include CN\(^-\), CHO\(_2\)\(^-\), C\(_2\)H\(_3\)O\(_2\)\(^-\), C\(_3\)H\(_3\)O\(_2\)\(^-\), PO\(_3\)\(^-\), HSO\(_4\)\(^-\), etc. after comparison, we know that there is strong K\(^+\) signal peak, CHO\(_2\)\(^-\), C\(_2\)H\(_3\)O\(_2\)\(^-\), C\(_3\)H\(_3\)O\(_2\) in the biomass burning source.

The characteristic elements in the positive spectrogram of the catering oil fume source (Figure 5) include Ca\(^+\) and its oxide, Fe\(^+\), Pb and organic carbon; there is NO\(_2\)\(^-\), NO\(_3\)\(^-\), PO\(_2\)\(^-\), PO\(_3\)\(^-\), HSO\(_4\)\(^-\), CN\(^-\), CNO\(^-\), Cl\(^-\), \(\text{OH}^+\), organic carbon and long-chain organic carbon etc. after comparison it is possible to judge that the typical components of the catering oil fume are Fe\(^+\), EC, organic carbon and long-chain organic carbon.

2.4. Correlation Analysis of Offline and Online Component Testing Result of Fine Particles Source Spectrum

To ensure the accuracy of the constructed particle dynamic source spectrum bank, we selected some typical pollution sources and carried out offline comparison sampling during the period of source spectrum collection and analysis, and compared with the analysis data of online source apportionment [8-10].
Table 1. Correlation analysis results

| Component | Dust source | R   | Correlation | Coal combustion source | R   | Correlation | Motor vehicle source | R   | Correlation |
|-----------|-------------|-----|-------------|------------------------|-----|-------------|----------------------|-----|-------------|
| K⁺        | 0.7         | good|             | K⁺                     | 0.75| good        | K⁺                   | 0.67| good        |
| Na⁺       | 0.68        | good|             | Na⁺                    | 0.64| good        | Na⁺                  | 0.65| good        |
| Si        | 0.75        | good|             | Ca²⁺                   | 0.58| good        | Ca²⁺                 | 0.56| good        |
| Mg²⁺      | 0.72        | good|             | Al³⁺                   | 0.64| good        | Mn²⁺                 | 0.53| good        |
| Ca²⁺      | 0.68        | good|             | Fe²⁺                   | 0.78| good        | EC                   | 0.78| good        |
| NO₂⁻      | 0.84        | highly|          | NO₂⁻                   | 0.74| good        | NO₂⁻                 | 0.76| good        |
| NO₃⁻      | 0.82        | highly|          | NO₃⁻                   | 0.79| good        | NO₃⁻                 | 0.74| good        |
| SO₄²⁻     | 0.76        | good|             | SO₄²⁻                  | 0.81| highly| Cl⁻                   | 0.66| good        |

After the correlation analysis of the mass concentration proportion of PM₂.₅ source spectrum off-line component and the particle number proportion of online source apportionment characteristic component, we finally acquired the result of pollution source spectrum as shown in Table 1. The correlation comparison result of the majority components present moderate positive correlation with highly correlation, therefore the online source apportionment of each category of pollutions possesses good representativeness and could qualitatively reflect the basic information of each category of pollution source and could act as the matching basis for the receptor sample of online source apportionment.

3. Empirical Research of Matching Diagnose

The matching diagnosis is based on fine particles source spectrum bank and match it with the online source apportionment data then it could reach the rapid diagnosis for air pollution status, and get the real-time components of pollutants, and increase the timeliness of handling heavy pollution weather. This research takes a heavy pollution process of Tianjin in December, 2015 as the example and utilizes online source apportionment technology to carry out matching diagnosis for the particles sources in the process of heavy air pollution.

Table 2. Changes in the chemical composition of the pollution process

| Heavy pollution process | PM₂.₅ concentration(μg/m³) | Chemical composition (%) |
|------------------------|----------------------------|--------------------------|
|                        | EC  | OC  | NH₄⁺ | Cl  | NO₂⁻/NO₃⁻ | HSO₄⁻ |
| Before pollution       | 53  | 5.5 | 30.4 | 4.5 | 17.1       | 40    |
| Mild pollution         | 94  | 5.3 | 27.2 | 4.7 | 2.9        | 16.9  |
| Moderately pollution   | 120 | 5.2 | 26.2 | 5   | 1.9        | 15.4  |
| Severe pollution       | 210 | 4.5 | 23.6 | 7.2 | 1.5        | 17.4  |
| After pollution        | 48  | 7.1 | 37.7 | 2.1 | 2.9        | 12.6  |

In the increasing process of pollutant, the proportion of organic matters and chloridion were gradually declined and the proportion of secondary inorganic salt ions (the sum of ammonium salt, nitrate and sulfate) presented an increasing trend. The proportion of secondary inorganic salt ions has increased 14% in heavy pollution status and its proportion dropped by 25% rapidly after the pollution which reflected that the pollution process was deeply affected by the regional pollutants and showed up the relative strong and continuous accumulative effect of secondary ions.

As for the variation status of particles source before pollution, in pollution and after pollution, the primary pollution sources before pollution are coal combustion, industry and motor vehicles exhaust; the primary pollution sources in the increasing process of PM₂.₅ concentration are industry and technology source and coal combustion source, among them the proportion of coal combustion source presents a small scale rising tendency, however the industry source presents a declining tendency; in heavy pollution periods the secondary inorganic source presents substantial increase and the largest
increasing range reaches up to 11.6% which could be resulted by the slow surface wind speed (level 0–2) of Tianjin during the pollution period which is not good for the local pollutant diffusion, in addition the higher relative humidity (60%–80%) would increase moisture absorption of particles and strengthen the accumulative effect of secondary inorganic ions concentration.

Table 3. Dyeing process sources of pollution changes

| Heavy pollution process | PM$_{2.5}$ Concentration (μg/m$^3$) | Chemical composition (%) |
|-------------------------|--------------------------------------|---------------------------|
|                         | Dust | Biomass burning | Motor vehicle | Coal combustion | Industry | Secondary | Others |
| Before pollution        | 53   | 6.3            | 5.5           | 18.4           | 24.3     | 21.5       | 10      | 14      |
| Mild pollution          | 94   | 5.8            | 3.6           | 17.7           | 20.5     | 27.3       | 8       | 17.1    |
| Moderately pollution    | 120  | 5.1            | 3.1           | 17.5           | 23.8     | 25.5       | 6.5     | 18.5    |
| Severe pollution        | 210  | 4.8            | 2.3           | 15.7           | 24       | 23.7       | 18.1    | 11.4    |
| After pollution         | 48   | 6.6            | 10.8          | 20.7           | 27.9     | 18         | 6.8     | 9.2     |

4. Conclusion
The online source apportionment of each category of pollutants has good representativeness and could qualitatively reflect the basic information of pollutant source and act as the matching basis for receptor sample of online source apportionment. After matching diagnosis research, we found that this time heavy pollution may be affected by meteorological factors and the accumulated local pollution sources. The continuous accumulative effect of secondary ions is relative strong in heavy pollution process. Starting the heavy pollution weather emergency alert could alleviate the seriousness of regional pollution.

Acknowledgments
This work was financially supported by National Science and Technology Support Program (2014BAC3B03) and Environmental protection commonweal research program (201409004) fund.

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