Spatial and temporal characteristics of PM2.5 and source apportionment in Wuhan

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Abstract. In order to study the pollution characteristics and sources of PM2.5, the PM2.5 in Wuhan atmosphere was sampled continuously. Inductively coupled plasma mass spectrometry (ICP-MS) were employed to measure Na, K, Mg, Ca, Al, Mn, Cu, Zn, As, Pb, Cr, Ni, Co, Cd, Fe, V, Ti, Hg, Si, while water soluble ions (Cl⁻, NO₃⁻, SO₄²⁻) as well as carbonaceous mass (EC and OC) were analyzed using ion chromatograph (IC) and carbon analyzer, respectively. The results show: (1) In 2014 and 2015, Wuhan PM2.5 values were 81.4μg/m³ and 69.2μg/m³, respectively far exceed the national standard level 2, i.e. annual average 35 μg/m³ in China, 10 μg/m³ by the World Health Organization, the annual limit of 15 μg/m³ in the United States. (2) Taking Huaqiao and Qihao as research points, the Spring Festival effect of PM2.5 in Wuhan city is analyzed. It shows that the concentration of PM2.5 in 2014 and 2015 is before Spring Festival> during Spring Festival> after Spring Festival. As a backdrop, during the Spring Festival, Qihao PM2.5 concentration than Huaqiao average low 20 μg/m³. (3) The results of positive factor matrix factorization (PMF) analysis show that PM2.5 in Summer in Wuhan mainly comes from the automobile source, soil dust source, biomass combustion, industrial source, secondary aerosol source, combustion coal source, the contribution rate is 37.7%. 25%, 16.4%, 8.1%, 6.5%, 6.4%, respectively.

1. Introduction

Atmospheric particulate matter (PM) is an important pollutant that affects the quality of ambient air in China [1]. China's traditional pollutants of sulfur dioxide (SO₂) and Total suspended particulate matter (TSP), although largely controlled, but PM2.5 (aerodynamic diameter ≤ 2.5 μm) has become a serious threat to people [2]. PM2.5 has the characteristics of small particle size, large surface area, strong activity, easy to be attached with toxic and harmful substances (for example, heavy metals and microorganisms), and has attracted worldwide attention due to their impact on human health [3-5], atmospheric visibility [6], balance of the Earth's radiation and climate [7].

PM2.5 source apportionment techniques include emission inventory method, source-oriented model method, and receptor model method [8]. Source-oriented model, also known as diffusion model method, which represents a simple model of AERMOD, ADMS, CALPUFF software [9], and complex models of Models-3 / CMAQ, NAQPSMS, CAMx, WRF-chem [10]. The receptor model mainly includes chemical mass balance model (CMB) and factor analysis model (PMF, PCA / MLR, UNMIX, ME2, etc.) [11].

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Currently, CMB model and positive matrix factorization (PMF) model are widely used. It should be noted that the CMB method has limitations in that it does not take into account the complexity of the source of PM in the ambient air and often encountered a set of data to get different source apportionment results [12-13]. Unlike the CMB model, which requires the collection of PM samples from source and the collection of PM samples from environmental acceptors, the PMF model is based on receptor chemical component data sets for source apportionment without source sample acquisition, and is highly recommended when sources are not formally known [14].

Wuhan is the core area of Wuhan city circle, urbanization and industrialization development have developed rapidly. Wuhan air pollution is more serious, frequent haze. 2013 "Wuhan Environmental Quality Bulletin" shows that the concentration of atmospheric PM2.5 exceeded the standard serious and PM2.5 is the primary pollutant in Wuhan. Thus, the major objectives of this paper are: (1) to characterize the spatial and temporal variations of PM2.5 in the period of 2014-2015 in Wuhan. (2) perform a comprehensive source apportionment of PM2.5 in Wuhan, China using US EPA PMF 5.0.

2. Materials and methods

2.1. Receptor sample collection for source apportionment

Based on the Wuhan environmental function zone, eight PM2.5 atmospheric environmental receptor sampling points were selected: Zhongshan Hospital, Hanyang District Government, Hankou Railway Station, Jiangan District, Qingshan District, Optical Valley Plaza, Yuemachang, Wuchang Railway Station (Figure 1).

![Map of the sampling sites in Wuhan](image)

Figure 1. Map of the sampling sites in Wuhan.

At each sampling point, the height of the sampler from the building roof is 10 meters. The sampling instrument is Laoyin 2050 PM2.5 sampler manufactured by Laoshan Electronic Equipment Company in Qingdao China, and the air flow rate fixed at 100 L/min. Sampling time June 1 - June 28, 2015, each lasting 24 hours and 82 samples were collected.

Sampler has two channels, respectively, placed quartz filter and teflon filter. The quartz filter sample was used for the analysis of water-soluble ions and carbon components, and the Teflon filter sample was used to analyze the elemental composition. The membranes were equilibrated at the same temperature and humidity for 24h before and after sampling, and weighed with a microbalance with a sensitivity of 1μg (Shimadzu, Japan) to determine PM2.5 mass concentrations by the difference in the weight of filters before and after sampling [15].

2.2. Sample analysis

An ICP-MS instrument (Model: NexIon 300X, Perkin Elmer Inc., US) was used for the analyses of 19 elements (Ti, Al, Mn, Ca, Mg, Na, K, Cu, Zn, As, Pb, Cr, Ni, Co, Cd, Hg, Fe, V and Si) in PM2.5 samples collected on Teflon filter. The ion chromatograph ICS-1100(DIONEX, US) was used to analyze Cl⁻, NO₃⁻ and SO₄²⁻. Organic carbon (OC)/elemental carbon (EC) were analyzed using a carbon analyzer (DRI Model 2001A, Atmoslytic Inc., Calabasas, CA, USA) following the
thermal/optical reflectance protocol [16]. A random sample of 10% of each sample was analyzed for parallel analysis. When the particles were collected and analyzed, the blank samples were added and the quality control measures were taken. At the same time, each of the analyzers was calibrated using standard substances, and the recoveries of each test substance were between 80% and 120%, reaching the quality control range.

2.3. Wuhan PM2.5 spatial and temporal distribution of concentration data source

In Wuhan, there are 10 national air quality observation stations and 10 municipal observation stations. Wuhan Municipal Environmental Protection Bureau has publicized a variety of air quality indicators (including PM10, PM2.5, CO, O₃, NO₂, SO₂) in a web platform (http://www.pm25.in/wuhan; http://ft.whepb.gov.cn:8090/Default.aspx). These air quality real-time distribution systems update data once an hour. PM2.5 data of Wuhan were collected for a 2-year period from 2014 to 2015 at the above 20 observation stations. It should be noted that these data are used to describe the temporal and spatial distribution of PM2.5 in Wuhan and the Spring Festival effect of PM2.5.

3. Results and discussion

3.1. PM2.5 temporal variations

In 2014 and 2015, Wuhan PM2.5 values were 81.4μg/m³ and 69.2μg/m³ respectively and far exceed the national standard level 2, i.e. annual average 35 μg/m³ according to Ambient Air Quality Standards (GB3095-2012) issued in 2012, let alone the air quality guideline of an annual average of 10 μg/m³ by the World Health Organization. For the PM2.5 daily average, 2014 and 2015, respectively, 52 days and 62 days less than 35μg/m3 (national standard level 1, the 24h air quality standard of China).

For the PM2.5 monthly mean (Figure 2), the maximum values are in January, the value in 2014 and 2015, respectively, 184 μg/m³ and 127.3μg/m³. The lowest value in 2014 and 2015 was found in August (43 μg/m³, 40.9 μg/m³ respectively).
The PM2.5 seasonal average concentration in Wuhan from 2014 to 2015 is shown in Figure 3. There is a clear seasonal variation in the PM2.5 seasonal average concentration in two complete years, which is basically the highest in winter and lowest in summer. The seasonal variation of PM2.5 was obvious. The seasonal variation of PM2.5 in Wuhan was in the order of winter (Dec.-Feb.) > spring (Mar.-May) > autumn (Sep.-Nov.) > summer (Jun.-Aug.). The PM2.5 concentrations had a U-shaped pattern of “high in autumn and winter but low in spring and summer” in the major cities of China [17].

Chinese New Year is an important traditional Chinese festival, during the Spring Festival, there is the custom of setting off firecrackers. In order to study the Spring Festival effect of Wuhan PM2.5, from the lunar New Year's Eve to the sixth day of the first month as the during Spring Festival (7d), the first 7d and the latter 7d as the control group, known as the non-Spring Festival period, thus mean PM2.5 concentration before, during and after the spring festival in 2014 and 2015 were calculated.

Figure 4. Mean PM2.5 concentration before, during and after the spring festival in 2014 and 2015.

The concentration of PM2.5 in 2014 and 2015 is before Spring Festival > during Spring Festival > after Spring Festival (Figure 4). Before the Spring Festival, industrial production activities carried out normally, making the overall level of pollution is high. During the Spring Festival, the production of industrial enterprises in a lot of cut-off, reduce pollutant emissions, atmospheric pollutants in the environment to reduce, resulting in air quality after the Spring Festival is better than during the Spring Festival and the before Spring Festival [18].

Figure 5. Diurnal variation of PM2.5 concentration during Spring Festival

In order to characterize the diurnal variation of PM2.5 in typical areas of Wuhan during Spring Festival, Qihao and Huaqiao were chosen as examples (Figure 5). Huaqiao is located in the main city of the Second Ring Road, the regional type of residential areas, traffic area, as the city representative point. Qihao located outside the city, as a control point. The concentration of PM2.5 increased significantly from 0:00 to 2:00 in the morning. PM2.5 concentration peaked at 10:00 AM and then decreased with the increase of daytime activities. As a backdrop, during the Spring Festival, Qihao PM2.5 concentration lowers than Huaqiao average 20 μg/m³.
3.2. PM2.5 spatial variations

According to Wuhan city layout planning [19], Wuhan City is divided into the central urban area (Wuhan urban area), the eastern area (Xinzhou district), the southern area (Jiangxia district), the western area (Dongxihu district, Caidian district), the northern region (Huangpi District).

Table 1. Seasonal distribution of PM2.5 in Wuhan (μg/m^3).

| Area          | Season       | Spring (Mar.-May) | Summer (Jun.-Aug.) | Autumn (Sept.-Nov.) | Winter (Dec.-Feb.) | Annual |
|---------------|--------------|-------------------|--------------------|---------------------|--------------------|--------|
| Central city  |              | 66.7              | 51.4               | 56.7                | 103.7              | 69.6   |
| Eastern region|              | 65.5              | 42.2               | 51.7                | 101.9              | 65.3   |
| Southern region|             | 56.4              | 60.4               | 65.0                | 93.2               | 68.8   |
| Western region|              | 64.4              | 61.7               | 59.3                | 99.0               | 71.1   |
| Northern region|             | 75.9              | 41.5               | 50.9                | 98.7               | 66.8   |

Figure 6. Annual Wuhan PM2.5 interpolation.

In spring, the concentration of PM2.5 in the northern area is higher than that in other areas, reaching 75.9μg/m^3. In summer, the concentration of PM2.5 in the west is 61.7μg/m^3, and in autumn the concentration of PM2.5 Value is 65.0μg/m^3 higher than that of other regions. In winter, the concentration of PM2.5 in the downtown area is 103.7μg/m^3, which is higher than other areas (Table 1)

From the annual average concentration, the western region 71.1μg/m^3 of PM2.5 concentration value, slightly higher than other regions. The PM2.5 value of the whole area is obviously decreasing from southwest to northeast, and PM2.5 is lower in the east and the north, higher in the west and south, and lower in the central area (Figure 6).

3.3. Analysis of spectral characteristics of PM2.5 samples

85 samples have been collected and elements, i.e., PM2.5, Cl, NO3-, SO42-, Na, K, Mg, Ca, Al, Mn, Cu, Zn, As, Pb, Cr, Ni, Co, Cd, Fe, V, Ti, Hg, Si, TC, OC and EC, were used to run PMF. Data below detection limit (BDL), half of the detection limit value was used; and for missing data, geometric mean of the measured concentrations for the same elements was used (Table 2).
Table 2. Mean, standard deviation, median and maximum concentration for PM2.5 samples.

| species | Maximum | SD   | Median | Mean  |
|---------|---------|------|--------|-------|
| PM2.5   | 62.2    | 22.0 | 35.7   | 60.5  |
| Cl      | 0.200   | 0.045| 0.200  | 0.128 |
| NO3⁻    | 4.355   | 0.701| 3.695  | 1.983 |
| SO4²⁻   | 12.464  | 1.582| 12.350 | 4.474 |
| Na      | 2.286   | 0.404| 2.130  | 1.142 |
| K       | 0.573   | 0.083| 0.560  | 0.236 |
| Mg      | 0.155   | 0.019| 0.135  | 0.054 |
| Ca      | 1.491   | 0.498| 1.110  | 1.408 |
| Al      | 0.272   | 0.054| 0.250  | 0.153 |
| Mn      | 0.040   | 0.006| 0.035  | 0.017 |
| Cu      | 0.0260  | 0.0111| 0.0135 | 0.0315 |
| Zn      | 0.2666  | 0.0408| 0.2340 | 0.1154 |
| As      | 0.0222  | 0.0095| 0.0100 | 0.0270 |
| Pb      | 0.0801  | 0.0189| 0.0636 | 0.0536 |
| Cr      | 0.0032  | 0.0005| 0.0033 | 0.0013 |
| Ni      | 0.0224  | 0.0101| 0.0108 | 0.0286 |
| Co      | 0.0002  | 0.0001| 0.0002 | 0.0002 |
| Cd      | 0.0030  | 0.0009| 0.0020 | 0.0024 |
| Fe      | 0.4549  | 0.0976| 0.3640 | 0.2759 |
| V       | 0.0024  | 0.0007| 0.0023 | 0.0019 |
| Ti      | 0.0093  | 0.0028| 0.0066 | 0.0078 |
| Hg      | 0.0008  | 0.0004| 0.0005 | 0.0010 |
| Si      | 0.6860  | 0.2485| 0.4225 | 0.7029 |
| TC      | 14.2788 | 1.5295| 14.7000| 4.3262 |
| OC      | 10.1825 | 1.1956| 9.6700 | 3.3816 |
| EC      | 4.0963  | 0.5111| 4.0100 | 1.4455 |

3.4. PMF model and source analysis results
The PMF model decomposes the original matrix X (n × m) into two factor matrices-g (n × p) and f (p × m) and a residual matrix e (i × j). Shows:

\[ e_{ij} = x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj} \] (1)

Where, \( x_{ij} \) - the j-th species mass measured in the i-th sample;
\( p \) - the number of factors;
\( g_{ik} \) - k-th source mass concentration contributing to the i-th sample.
\( f_{kj} \) - j-th species mass fraction from the k-th source

The elements in matrices g and f are all positive values, that is, they are non-negatively restricted. Factor contributions and profiles are derived by the PMF model minimizing the objective function Q:

\[ Q = \sum_{i=1}^{n} \sum_{j=1}^{m} (e_{ij}/u_{ij})^{2} \] (2)
Where: \( u_{ij} \) the uncertainty of the jth chemical component in the ith sample; PMF can accept two methods of calculation of uncertainty: an observation-based method; a equation-based method.

Computational Uncertainty Computation:

When the concentration of the component is below the detection limit:

\[
Unc = MDL \times \frac{5}{6}
\]

When the component is above the concentration detection limit:

\[
Unc = \sqrt{\left(\text{Error Fraction} \times \text{concentration}\right)^2 + \left(0.5 \times MDL\right)^2}
\]

Where, Unc for the uncertainty, MDL for the instrument minimum detection limit; Error Fraction is expressed as a percentage of the measurement uncertainty.

In this study, EPA PMF5.0 software was used for analysis. A total of 85 valid environmental receptor samples were involved in the model calculation. The number of samples involved in the calculation exceeds minimum number of samples is 45 \( \cdot \). The model input files are: (1) PM2.5 mass concentration and 25 chemical components; (2) Uncertainty data for each component.

In the PMF model calculation, try 4-9 factors to find the optimal number of factors. Finally, six factors, i.e., automobile source, soil dust source, biomass combustion source, industrial source secondary aerosol source, combustion coal source can be reasonably explained. And the analytical result is stable; most residual values are distributed between -3 and +3. The Fpeak value was adjusted between -5 and +5, and the space of factor rotation was found. When the Fpeak value was -0.5, the Q value was the smallest, so the analysis result of PMF was selected when Fpeak = -0.5.

Factor 1 represents the source of industrial source. Fe, Zn, Pb are the characteristic elements of some metal manufacturing industry, representing the source of metal metallurgy. Fe, Mn is a characteristic element of some ferrous metals manufacturing industry, Cu, Zn, Pb on behalf of non-ferrous metallurgy sources [20].

Factor 2 represents the source of secondarily formed aerosol source \( \text{SO}_4^{2-} \), K and Al concentrations are very high, and the importance of EC and metal elements is low, it can be considered from the secondary sources of atmospheric fine particles formed in the photochemical reaction.

Factor 3 represents the source of combustion coal source. Cl, F, Fe, Cr and Hg are a tracer of coal burning [15, 21].

Factor 4 represents the source of soil dust with typical crust elements, i.e., Mn, Mg, Ca, and Ti, including soil particles and fugitive dust as presented in Figure 7. The attributable indicators associated with this profile clearly support the existence of soil and dust re-suspension sources [22, 23]. According to incomplete statistics, Wuhan City, about 10,000 construction sites at the same time construction.

Factor 5 represents the source of biomass combustion. It can be seen from the source profile that the importance of K is the highest and the concentration of OC is high. Yu et al., (2013) published that biomass burning indicator was K [24].

Factor 6 represents the source of automobile source. In this factor, OC, EC, Fe, Al, Cu, and Zn concentrations and importance are greater. EC and OC are released from vehicle exhaust [25]. Mazzei et al., (2008) found indicators of traffic as Cu, Zn, and Pb [26]. In the car brake, the brake friction to release Cu, tires and ground friction, will release the Zn [27].

Figure 8 shows the estimated contribution results of PM2.5 source apportionment in Wuhan. It can be seen that the greatest contributor to the mass concentration of PM2.5 is the automobile source (37.7%), soil dust contribution to the PM2.5 of 24%, followed by 16.6% for biomass combustion, 8.3% for industrial source, 6.5% for secondary aerosol source and 6.4% for combustion coal.

It is very important to determine the indicators in the receptor model. So-called indicators are those that can characterize the source characteristics and do not change much in the course of atmospheric transport. It is an important to identify and trace potential sources. Because of the different source classification, the selection of indcotor is not the same.

In the previous study, Wuhan PM2.5 source analysis showed that the main sources of pollution from coal and motor vehicle emissions. Wuhan PM2.5 sample source analysis in summer shows that
the main sources of pollution from traffic sources (29%), road dust (27%) (Xiao et al., 2013). The analysis of PM2.5 sources in winter in Wuhan has revealed that 28.6% of the sources, 27.1% of the industrial sources [27]. In this study, the PM2.5 sampling period was in spring, the source of traffic was 37.7% and the dust was 24%.

With the rapid development of China's urbanization process, the city size and population are expanding, the number of urban vehicles is increasing year by year, the traffic source has become another major source of urban PM2.5. A large number of research results show that the main sources of fine particle pollution in urban air are coal combustion, motor vehicle exhaust, dust, industrial dust, secondary particles, biomass combustion, organic matter and sea salt particles.

Figure 7. Source profiles of PM2.5 in Wuhan city analyzed by PMF model.
4. Conclusion
The seasonal variation of PM2.5 concentration in Wuhan was as follows: winter> spring> autumn> summer. The average concentration of PM2.5 was 81.4μg/m³ in 2014 and 69.2μg/m³ in 2015 respectively.

The PM2.5 concentration in Wuhan has a Spring Festival effect. During the Spring Festival, the practice of setting off firecrackers has an adverse effect on Wuhan PM2.5, the Government should implement the "ban on whipping", or the division of the region to plan a whip.

By using EPA PMF 5.0, a source apportionment study of PM2.5 samples was carried out. Six main sources of PM2.5 in Wuhan were obtained: the automobile source, soil dust, biomass combustion, industrial source, secondary aerosol source, combustion coal. The corresponding contribution rate is 37.7%, 25%, 16.4%, 8.1%, 6.5% and 6.4%, respectively. Wuhan needs to actively adjust its energy structure, introduce advanced technologies and reduce the total amount of coal, while speeding up the elimination of backward production capacity and promoting the industrial transformation and upgrading.

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