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Long-term variation of the levels, compositions and sources of size-resolved particulate matter in a megacity in China

Ying-Ze Tian [a], Jian-Hui Wu [a], Guo-Liang Shi [a,*], Jian-Yu Wu [a], Yu-Fen Zhang [a], Lai-Dong Zhou [b], Pu Zhang [b], Yin-Chang Feng [a]

[a] State Environmental Protection Key Laboratory of Urban Ambient Air Particulate Matter Pollution Prevention and Control, College of Environmental Science and Engineering, Nankai University, Tianjin 300071, China
[b] Chengdu Research Academy of Environmental Sciences, China

HIGHLIGHTS

- Long-term monitoring of PM_{10} and $PM_{2.5}$ was carried out in a megacity in China.
- Long-term trends of levels, size distribution, composition and sources of PM were investigated.
- Sources of size-resolved PM were quantified by PMF.
- PMF–HCA was performed to identify periods influenced by different dominant sources.

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ABSTRACT

To investigate the long-term trends and variations of the levels, compositions, size distribution and sources of particulate matter (PM), long-term monitoring campaigns of PM_{10} and $PM_{2.5}$ were performed in a megacity in China (Chengdu) during the period from 2009 to 2011. The average concentration of PM_{10} was 172.01 ± 89.80 μg/m^3 and that of $PM_{2.5}$ was 103.15 ± 59.83 μg/m^3, with an average $PM_{2.5}/PM_{10}$ of 0.60. Enrichments of the important species indicated that the fractions of crustal elements were higher in PM_{10} than those in $PM_{2.5}$, while the abundance of organic carbon (OC) and secondary ions was enriched in the fine PM. Quantitative source apportionments of both PM_{10} and $PM_{2.5}$ were performed by PMF. PM_{10} and $PM_{2.5}$ in Chengdu were influenced by similar source categories, and their percentage contributions were in the same order: crustal dust was the highest contributor, followed by vehicular exhaust, secondary sulfate, secondary nitrate and cement dust. Crustal dust and cement dust contributed a higher percentage to PM_{10} than to $PM_{2.5}$, while vehicular exhaust and secondary particles provided higher percentage contributions to $PM_{2.5}$. In addition, PMF–HCA was performed to investigate the characteristics of the sources of the clustered samples, identifying three periods: crustal dust dominant-period, secondary sulfate dominant-period and comprehensive source influenced-period. Planting, reduction of precursors, and banning high-emission vehicles should be implemented to control crustal dust, secondary particles and vehicular exhaust in Chengdu. Furthermore, the size-resolved and the period-resolved control would be more effective.

1. Introduction

Atmospheric particulate matter (PM) is one of the primary concerns in megacities, due to their association with health effects and environment problems (Zheng et al., 2007; Tie and Cao, 2009; Koçak et al., 2011; Díaz et al., 2012; Maenhaut et al., 2012). PM_{10} is defined as PM with an aerodynamic diameter less than 10 μm, and $PM_{2.5}$ is defined as PM with an aerodynamic diameter less than 2.5 μm. Considering their adverse impact on human health, climate change, visibility and so on (Tie et al., 2009; Cao et al., 2012; Zhang et al., 2012), legislation defining PM_{10} and $PM_{2.5}$ concentration limits has been established by many countries. Monitoring of PM_{10} and $PM_{2.5}$ plays a pivotal role in investigating the levels, composition, size distribution and sources of PM, and long-term monitoring can help researchers to study the long-term trends and the variations in the characteristics of PM.

In addition, understanding the sources of size-resolved PM is pivotal for strategy-makers to effectively control and manage the PM pollution (Ali et al., 2012; Chen et al., 2012). Source apportionment of PM has been used to identify source categories and quantify source contributions all over the world (Pancras et al., 2011; Zheng et al., 2011; Xu et al., 2013). Source apportionment studies have determined that the characteristics of compositions and sources of

* Corresponding author. Tel.: +86 22 23507962; fax: +86 22 23503397.
E-mail address: nksgl@hotmail.com (G.-L. Shi).

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PM_{10} and $PM_{2.5}$ are different (Almeida et al., 2006; Karanasiou et al., 2009), so synchronous monitoring of PM_{10} and $PM_{2.5}$ is required and size-resolved source apportionment is critical for further studies of PM_{10} and $PM_{2.5}$. In addition, features of sources and dominant sources in different periods are different. Analyzing datasets of long-term monitoring is a powerful tool for observing the long-term variations of the sources and the dominant sources in different periods. However, data from such a synchronous and long-term monitoring of both PM_{10} and $PM_{2.5}$ is very scarce in developing countries, especially in China.

To investigate the long-term trends and variations of the levels, compositions, size distribution and sources of PM_{10} and $PM_{2.5}$, campaigns of long-term monitoring of PM_{10} and $PM_{2.5}$ were performed in a megacity (Chengdu) in China. First, the levels and compositions of PM_{10} and $PM_{2.5}$ were investigated. Second, the sources of both PM_{10} and $PM_{2.5}$ were quantitatively apportioned by Positive Matrix Factorization (PMF). PMF is sanctioned by the U.S. Environmental Protection Agency (EPA) and has been widely applied (Tian et al., 2013a; Yang et al., 2013). PMF is a factor analysis method constraining factor loadings and scores to non-negative values. PMF does not require information on source profiles and requires a large number of samples, so it is suitable for long-term monitoring studies. Finally, a new method, PMF–HCA (PMF–hierarchical cluster analysis), was employed to classify the PM samples and investigate the dominant sources during different periods. As far as we know, the effort to apply PMF–HCA for the identification of periods that were influenced by different dominant sources is very rare. The objectives of this work were to: (1) investigate the long-term trends and variations of the levels, compositions, size distribution and sources of PM in Chengdu; and (2) study the characteristics of the sources for size-resolved PM and for different dominant source-periods, to provide useful information for control policies in diverse PM pollution periods.

2. Materials and methods

2.1. Sampling

In this work, PM_{10} and $PM_{2.5}$ samples were collected in a megacity in China — Chengdu. As shown in Fig. S1, Chengdu (102°54′–104°53′ E, 30°05′–31°26′N), the capital of Sichuan Province, is one of the most important economic, transportation and communication centers in Southwest China. The area of Chengdu is 12,121 km^2 and the population of the city is over 10 million. Chengdu has a monsoon-influenced humid subtropical climate and distinct seasons with abundant rainfall throughout the year, as well as sweltering summers and freezing winters. The favorable climate and fertile soil make Chengdu known as the home of giant pandas.

Ambient PM_{10} and $PM_{2.5}$ samples were collected from 2009 to 2011 at the building of Environmental Protection Agency (104°04′E, 30°35 N′) in Chengdu. PM_{10} and $PM_{2.5}$ samples were collected by filter-based samplers. For both PM_{10} and $PM_{2.5}$, two parallel medium-volume air samplers were used, one for polypropylene membrane filters and the other for quartz-fiber filters. The pumps were set at 100 L/min and ran continuously for 24 h. After the sampling campaign, a total of 141 PM_{10} samples and 152 $PM_{2.5}$ samples were obtained within the sampling period.

2.2. Chemical analysis

The elements (Na, Mg, Al, Si, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Cd and Pb) in the ambient samples collected on polypropylene membrane filters were analyzed by Inductively Coupled Plasma (IRIS Intrepid II, Thermo Electron). PM_{10} and $PM_{2.5}$ samples collected on quartz-fiber filters were used to analyze the water soluble ions and carbon species. Water soluble ions (NH_4^+, NO_3^- and SO_4^{2-}) were extracted by an ultrasonic extraction system (AS3120, AutoScience) and analyzed by ion chromatography (DX-120, DIONEX). The level of organic carbon (OC) was determined by DRI/OGC carbon analyzers following the IMPROVE thermal/optical reflectance (TOR) protocol.

The detailed descriptions of the sampling, chemical analysis and quality assurance/quality control are provided in the SUPPLEMENTARY materials and in our previous works (Shi et al., 2009a; Xue et al., 2010).

2.3. Positive Matrix Factorization (PMF)

PMF attempts to apportion the source profile matrix F (p × j) and the source contribution matrix G (i × p) on the basis of observations at the receptor site with the constraint of limiting F and G to non-negative values:

$$x_{ij} = \sum_{h=1}^{p} g_{ih} f_{hj} + e_{ij} \tag{1}$$

where x_{ij} is the jth elemental concentration measured in the ith sample; f_{hj} (μg/μg) is the fraction of the jth element in the hth source and is constrained to non-negative values in PMF; g_{ih} is the contribution of the hth source to the ith sample and is also constrained to non-negative values; e_{ij} is the residuals; and p is the number of factors extracted (Paatero, 2007; Wagenera et al., 2012).

The task of PMF is to minimize an 'object function' Q defined as:

$$Q(E) = \sum_{i=1}^{m} \sum_{j=1}^{n} \left(e_{ij}/\sigma_{ij}\right)^2 \tag{2}$$

where the value σ_{ij} is the "uncertainty" in the jth species for the ith sample, which is used to down weight the observations that include sampling errors, detection limits, missing data, and outliers (Paatero, 2007).

In this work, PMF was performed on a matrix made up of 20 columns (number of chemical species) and 141 rows (number of PM_{10} samples) for PM_{10} and on a matrix of 20 columns (number of chemical species) and 152 rows (number of $PM_{2.5}$ samples) for $PM_{2.5}$. Selecting the number of factors and FPEAK are two important issues for choosing between the different possible solutions of PMF. In this study, different numbers of factors and different FPEAK values were tested. Considering the performance of PMF and the Q values (the theoretical Q for a model run is equal to $nm - p(n + m)$) (Paatero et al., 2002), five factors and FPEAK = 0 were assigned for the model fittings of both PM_{10} and $PM_{2.5}$. What's more, the PMF implementations were set to repeat ten times from ten pseudo-random starting points, to test if a global minimum solution was achieved. Robust mode and EM = −14 were chosen in this work which are recommended for general-purpose environmental works (Paatero, 2007). The uncertainties required by PMF were calculated according to the equation recommended in User's Guide for PMF (Paatero, 2007):

$$\text{std} - \text{dev}\left(x_{ij}\right) = 5\% \text{ of } x_{ij} \text{ plus two units of the least significant digit reported for } x_{ij}.$$

2.4. HCA and PMF–HCA

Hierarchical clustering analysis (HCA) is a statistical method to classify samples into clusters through their similarity and different cluster rules. In this work, the HCA was implemented in SPSS 16.0, using Ward's Hierarchical agglomerative method of clustering and Euclidean distance measure (Masiol et al., 2010; Li et al., 2012), to analyze the relationships among the chemical species in PM_{10} and $PM_{2.5}$. Furthermore, PMF–hierarchical cluster analysis (PMF–HCA) was used to classify the samples according to their similarity on source contributions. PMF–HCA combines the results of PMF with