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Original article

Distribution patterns and characterization of outdoor fine and coarse particles

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Simultaneous measurements of fine ($PM_{2.5}$) and coarse (PM_{10}) particles have been performed during three sampling period: summertime, early winter before the heating period, and during the winter heating. The sampling was done at an urban site, Harbin City, China, to apportion pollution sources and to investigate the impacts of weather parameters and emission sources on distribution patterns of $PM_{2.5}$ and PM_{10} and their chemical compositions. Two chemometric techniques, hierarchical clustering analysis (HCA) and discriminant analysis (DA), and a receptor model (PMF5) were applied. The average mass concentrations of fine and coarse particles during the whole study period (i.e. annual averages), were 82.4 μg/m^3 and 120.1 μg/m^3, with relative humidity and wind speed being the main factors influencing distribution patterns of $PM_{2.5}$ and $PM_{10,}$ while sum of major ions (NO_3^-, NH_4^+, SO_4^{2-}), and organic carbon (OC) were the greater contributor to total mass concentrations. According to DA, the distribution patterns of $PM_{2.5}$ and PM_{10} during the winter heating period were distinct but overlapping in summer and early winter before heating, implying that, $PM_{2.5}$ and PM_{10} were originated from different sources during the winter heating period but from similar sources during the other two sampling periods. This claim was further supported by PMF results. Canonical discriminant function coefficients of DA have shown species such as OC, EC, SO_4^{2-}, NO_3^-, Cl^-, Ti, Sr, Ca^{2+}, Ni, and Ba to be good predictors/discriminants responsible for the differences between the three sampling periods. HCA visualized the interrelations among the source markers, while the PMF5 modeling confirmed HCA findings.

1. Introduction

Atmospheric particulate matter was described as a mixture of solid and liquid chemical species that originated from either natural or anthropogenic sources (Aldabe et al., 2011; Herrera Murillo et al., 2012). Exposure to particulate matter, especially the fine particles ($PM_{2.5}$), has been linked with many harmful health endpoints. Examples of these harmful effects include: pneumonia and bronchitis in children (Jedrychowski et al., 2013), pulmonary inflammation (Ding et al., 2010; Happo et al., 2010), respiratory mortality (Li et al., 2013a), and different cardiopulmonary and toxicological effects (Pope et al., 2004; Schins et al., 2004; Schneider et al., 2008; Allen et al., 2009; Liao et al., 2010; Feng and Yang, 2012; Strak et al., 2012; Wang et al., 2013; Cachon et al., 2014).

Owing to rapid urbanization, growing demand for energy, increased use of automobiles, and wide-scale biomass burning, air pollution in China has become a serious environmental issue (Zhao et al.; Pui et al., 2014; Zhu et al., 2015). Vehicle density in the country was expected to increase from 50 to 140 vehicles per 1000 population from 2010 to 2030 (Gajendra Babu and Subramanian, 2013). This trend, coupled with continuous utilization of large amounts of coal for central heating, complicates the control of

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smog. Coal combustion represents approximately 70% of primary energy consumption in China, with coal principally used for winter heating and household cooking (Zhang et al., 2008). In addition, more air pollutants are expected to be released from industrial development (Wang and Hao, 2012; Duan and Tan, 2013; Lutgens and Tarbuck, 2013). Although fuel efficiency policies (such as adoption of fuel economy standards) and use of environmentally-friendly vehicles will positively contribute to minimize certain emissions (Gajendra Babu and Subramanian, 2013), more control measures are needed to reduce levels of $PM_{2.5}$ in air (Song et al., 2007; Wang and Hao, 2012).

A limited number of studies have investigated and apportioned the sources of $PM_{2.5}$ in places like Harbin, China, where the ambient temperature is very low in winter, and the city is surrounded by agricultural fields where massive biomass burning takes place during late autumn and beginning of winter. Emissions and cool air are suggested to be trapped due to effects of meteorological conditions such as an inversion layer. Add to that, there are several hundred of factories such as pharmaceutical factories around the city. It has to be mentioned also that, DA and hierarchical clustering analysis (HCA) have been intensively applied in biological sciences, analytical chemistry and water quality studies. However, only a limited number of studies have applied them in the study of particulate matter possibly due to availability of several emission and receptor models and difficulty in interpreting results of HCA sometimes. The major goals of this study were: to apportion the potential sources of $PM_{2.5}$ and PM_{10}, through application of advanced receptor Positive Matrix Factorization (PMF, v.5) model, along with HCA; to investigate the chemical species that have the higher impact on group discrimination; to estimate possible influence of weather conditions on the particles' distribution patterns; and to show the similarity in trends of $PM_{2.5}$ and PM_{10}.

Discriminant analysis (DA), one of the *supervised pattern recognition* techniques (Miller and Miller, 2005), is an approach that could be applied to accomplish two major functions, namely, prediction (or classification) and description (or explanation), i.e. describing group differences and discovering the predictors that discriminate/differentiate between groups (Singh et al., 2004; Meyers et al., 2013). DA requires certain assumptions to be fulfilled. For instance, low multicollinearity of the predictors/independent variables, absence of outliers in the data set and multivariate normal distribution of the variables. There are different types of DA analysis, the most common of which are: *linear discriminant analysis* (LDA) and *quadratic discriminant analysis* (QDA). The performance of the model is checked through *cross-validation*, or the "leave one out method" (Miller and Miller, 2005). Commonly, (optional) canonical variate analysis (CVA), an extension of LDA, is applied. Unlike hierarchical clustering analysis (HCA), DA achieves classification with prior knowledge of membership of objects, for instance, grouping according to sampling sites or sampling campaigns is known (Retnam et al., 2013).

On the other hand, hierarchical clustering analysis is considered as an easy understandable technique that visualizes membership among objects and sample groups in form of nested clusters, which is arranged as dendrogram or a tree (Melon and Milite, 2012). It has been suggested as a useful technique for confirming results of other multivariate techniques. However, it has rather limited applications in studies on atmospheric particulate matter due to a potential difficulty in interpreting the dendrogram (Prendes et al., 1999; Ho et al., 2006; Contini et al., 2012).

2. Materials and methods

2.1. Study area and sampling

The monitoring site was situated on a building's rooftop approximately 12 m from the ground, in Harbin (44°04′ N to 46°40′ N north longitude; 125°42′ E to 130°10′ E east Longitude), a city with 5.6 °C mean annual ambient temperature to the northeast china (Li et al., 2014). The city characterized with very cold winter (Oct. to Apr.) where the temperature commonly drops below zero in October until beginning of April. The present study was done during three sampling periods, as shown in Table 1. Every campaign extended for four consecutive weeks. A number of 90 $PM_{2.5}$ and 90 PM_{10} samples were collected on Quartz filter utilizing medium-volume aerosol sampler (Model, Laoying 2030, Laoshan Corporation, Qingdao, China) at a flow rate of 100 l/min for twenty-four hours each day. Before starting sampling, all filters were thermally treated (450 °C; 8 h) in an oven. Subsequently, samples were neutralized in desiccators for 24–48 h at 25 ± 5 °C and 35 ± 5 relative humidity (RH) then subjected to gravimetric analysis with sensitive microbalance before the chemical analysis. A number of 26 blank samples were also analyzed for quality assurance.

2.2. Chemical analysis

To perform different chemical analysis, each quartz filter (27.92 cm^2 total area) was cut into four pieces, each for one type of analysis. To analyze water soluble ions, one-quarter of the quartz filter was extracted ultrasonically using ultrasonic water bath and deionized water filtered through a water filter (Model D111911, *NANOpure Diamond,* Barnstead International company, U.S.). Extraction was done twice for each filter, each time using 20 ml of the deionized water (at a temperature of 30 °C for one hour). Subsequently, extractes were filtered via fine filter (0.45 μ) and injected into ion chromatography (Model ICS-90, Thermo scientific, Inc. USA) (Li et al., 2012).

A thermal/optical carbon analyzer (desert research institute, model 2001, Atmoslytic Inc., USA) was used for analyzing organic carbon (OC) and elemental carbon (EC) through applying Interagency Monitoring of Protected Visual Environments Advanced (IMPROVE_A) protocol. Details of IMPROVE_A protocol and the instrument temperature program were stated in other studies (Cheng et al., 2011; Chow et al., 2011; Yau et al., 2013). For the analysis, small piece (o.53 cm^2) from each sample filter was taken. Finally, for heavy metal analysis, filters were first subjected to microwave-assisted acid digestion with strong acid (Nitric acid-HNO_3), assisted by hydrogen peroxide (Bajo, 1991), then analyzed with Inductively Coupled Plasma Mass Spectrometer (ICP-MS) [Model: X series 2, ICP-MS, Thermo Fisher, corporation, U.S.A.].

2.3. PMF modeling and statistical analysis

The PMF5 software, an upgraded version of PMF2 developed by Environmental protection Agency (EPA), was applied. This new version has several advantages over the previous versions (PMF2 & PMF3) (Norris et al., 2014) for instance, only values of concentrations greater than the uncertainty contribute to the signal portion that used in the Signal/Noise (S/N) calculation. Another interesting feature of PMF5, is that, out of the converged solutions, the model automatically highlights the best one to be further investigated or simply researchers could investigate all of these converged ones. The best solution refers to results of a single run of the modeling that gives the lowest value of Q (robust) (Karnae and John, 2011;