Atmospheric Pollution Research 7 (2016) 547–556

Contents lists available at ScienceDirect

Atmospheric Pollution Research

journal homepage: http://www.journals.elsevier.com/locate/apr

Original article

Source identification of trace elements in the atmosphere during the second Asian Youth Games in Nanjing, China: Influence of control measures on air quality

Lu Qi, Yafei Zhang, Yinghui Ma, Mindong Chen*, Xinlei Ge**, Yan Ma, Jun Zheng, Zhen Wang, Shizheng Li

School of Environmental Science and Engineering, Nanjing University of Information Science &Technology, Jiangsu Key Laboratory of Atmospheric Environment Monitoring and Pollution Control, Collaborative Innovation Center of Atmospheric Environment and Equipment Technology, Nanjing 210044, China

ARTICLE INFO

Article history:
Received 13 August 2015
Accepted 11 January 2016
Available online 4 February 2016

Keywords:
Trace elements
Control measures
Source identification
PMF

ABSTRACT

An intensive field campaign was carried out at Nanjing Bureau of Meteorology located on the Jiangxin island during July 28-Aug 30, 2013. Concentrations of 15 trace metal elements (Al, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Sr, Cd, Ba, Pb Pd) were measured in the daily collected $PM_{2.5}$ filter samples by the inductively coupled plasma mass spectrometry (ICP-MS). Mass loading of Zn was found to be higher than other elements, even higher than Al, indicating that the airborne Zn in this region may have multiple sources including traffic emissions, emissions from ship paintings and ship-fuel burning. Six sources, which are coal combustion, soil dust, traffic, industry, electroplate and electronic pollution, and Cr source were identified by combining positive matrix factorization (PMF) analysis and the control measures of air quality during the Asian Youth Games (Aug 16–24, 2013, "control period"). Source contributions from coal combustion and industry were obviously reduced during the control period, while contributions from traffic, electronic pollution and Cr source increased, indicating the importance of the specific pollutants due to anthropogenic activities. Based on the meteorological data and air mass back trajectories, air parcels originated from southeast direction may deliver pollutants from industrial emissions containing elements of Co, Zn, Cd, Ba, Pb and Pd, while the air masses arriving in Nanjing from directions of Fujian and Zhejiang provinces contained high concentrations of As, Sr, and Cu, likely from combustion sources.

1. Introduction

Atmospheric trace metal elements are released into atmosphere from both natural and anthropogenic sources. They can enter into human body via inhalation, ingestion and dermal contact, then deposit in body. These trace elements also have potential risks by causing chronic disease, lung and heart disease, cancer to human health (Chen et al., 2011; Cohen, 2013; Hu et al., 2012; Lü et al., 2009; Peled, 2011; Pope III et al., 2002). Most elements are chemically stable and non-volatile, thus can stay in the atmosphere for a long time, and be transported or dispersed across a range of hundreds to thousands kilometers (Moreno et al., 2012; Pan et al., 2013; Senlin et al., 2008). The removal process from atmosphere for these elements include both dry and wet depositions, so they can also exert adverse effects on the cycles of terrestrial and coastal ecosystems (Cizmecioglu and Muezzinoglu, 2008; Soriano et al., 2012). Countries like USA, UK, even all European countries have built routine monitoring networks for trace elements in the atmosphere, but insufficient attention has been paid to this issue in China, and even less in Nanjing (Duan et al., 2014; Witt et al., 2010). For the evaluation of atmospheric transport of air pollutants, the source identification of trace elements is required.

* Corresponding author.
** Corresponding author.
E-mail addresses: chenmdnuist@163.com, my.lailai@163.com (M. Chen), caxinra@163.com (X. Ge).

Peer review under responsibility of Turkish National Committee for Air Pollution Research and Control.

http://dx.doi.org/10.1016/j.apr.2016.01.003

On a mass basis, trace elements represent a minor fraction in atmospheric aerosol, but they can act as specific tracers to identify major sources of the aerosols (Pan et al., 2013; Pancras et al., 2013; Richard et al., 2011; Zhou et al., 2014). The relative importance of the sources of airborne trace elements has already been discussed, especially at urban cities and industrial regions (Lee et al., 2007; Nazir et al., 2011; Pui et al., 2014; Saffari et al., 2013). It has been well documented that trace elements like nickel (Ni), chromium (Cr), vanadium (V), zinc (Zn), cobalt (Co) can be emitted from sources of industrial and fossil fuel combustion (Chen et al., 2013; Li et al., 2013); manganese (Mn), lead (Pb), barium (Ba), copper (Cu), zinc (Zn) are the tracers of traffic emissions (Bukowiecki et al., 2009; Zhang et al., 2009); Arsenic (As), strontium (Sr), selenium (Se) are produced from coal combustion (Makkonen et al., 2010); Aluminum (Al) and magnesium are identified as the tracers of soil or dust (Pavuluri et al., 2013). In recent years, the advanced positive matrix factorization (PMF) method has been applied to assess trace elements' sources in a few developed countries (Qin et al., 2006; Rizzo and Scheff, 2007; Yang et al., 2013). This model can provide source profiles of the major sources and quantify the mass contribution of each source. However, very few source apportionment studies regarding the trace elements of aerosols were conducted in Nanjing, even though the influences of heavy metals are well recognized and such studies may provide a better insight into the control measures for the reduction of air pollution.

In this study, we present source apportionment of trace elements in atmospheric aerosols collected during an intensive field campaign (July 18-Aug 30,2013) which covered the period of Asian Youth Games (August 16, 2013−August 24, 2013) in Nanjing. During this special month, the government had strict emission controls on the industrial activities, traffic and other emission sources, which can directly alter the source profiles of the trace elements than usual, and may also present some particular source information. Thus a combined discussion on the results from the PMF analysis and influences of the control measures can be very valuable. 15 trace elements were chosen in this study; PMF was applied to identify the possible source due to the advantage that it can be used without knowing a prior source composition; Influence of the air mass transport was analyzed combining with meteorological data as well.

2. Materials and methods

2.1. Site description

Aerosol samples were collected at Nanjing Bureau of Meteorology (32.04°N, 118.70°E) from July 28, 2013 to Aug 30, 2013. Nanjing is an industrial city, the capital of Jiangsu province in eastern China (Fig. 1). The sampling site is located on the Jiangxin island, about 100m to the east coast of riverbank of Yangtze river. It is 3 km southeast of the Olympic Sports Center. This site is characterized by the background-like nature with low pollutants.

2.2. Sampling and pre-treatment of samples

In total, Forty-two $PM_{2.5}$ samples were collected daily during the campaign. Quartz microfiber filters (9 cm, 100 circles, Whatman, UK) were used for sample collection. A medium volume sampler (HY-100, Qingdao Hengyuan Instruments Co. Ltd. Qingdao, China) with a sampling flow rate of 100 L/min was used to collect $PM_{2.5}$ samples at this site. The sampling frequency was 12h (from 8:00 in the morning to 20:00; from 20:00 to 8:00 the following day). Meteorological parameters were recorded at the meteorological station very close to the site. Before sampling, filter blanks were heated in the muffle furnace for five hours at 500 °C, then were stored in a chamber at constant temperature (25 °C) and relative humidity (45%) before use. Before and after collection, we use a digital balance (precision: 10^{-5} g) to measure the mass of filters and calculated the $PM_{2.5}$ mass loading of each sample.

2.3. Chemical analysis by the ICP-MS

Microwave digestion was applied for the destructions of metal elements. 1/8 of the filters were acid digested in a mixture of HNO_3 (69%, 5 ml) and HF (1 ml) by a microwave digest system (MARS 6, CEM Corporation, USA). The digestion process includes three steps. The first step is to raise temperature to 190 °C in 20min; the second step is to maintain the samples at 190 °C for 25min for a complete digestion; and the last step is to cool down in 30min. Then, the digestion solution was diluted to 45 ml with Milli-Q water to insure the solution acidity below 10%. All samples solutions were stored at 4 °C before analyses.

The concentrations of Al, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Sr, Cd, Ba, Pb in the digestion solution were determined by using the Thermo X2 Series Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Thermo, USA). The parameter and sensitivity of the instrument were calibrated daily according to the standard protocols. External standard (2 ppb, 5 ppb, 10 ppb, 18 ppb) and internal standard (2 ppb, In) were applied to calibrate the concentrations of trace elements.

Blank samples and two standard reference materials GBW07403, GBW08401 were digested in the same way as the samples, then analyzed by ICP-MS. The mean values of blank filters of Al, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Sr, Cd, Ba, Pb, Pd were 16.8, 0.15, 1.2, 0.55, 3.36. 0.3, 0.12, 1.57, 0.85, 0.11, 0.03, 0.08, 0.25, 0.06, 0.01 ng/m^3. All the results showed below were subtracted by the blank values. The detection limits (three times the standard deviation of the blanks analyzed) were Al (0.28 ng/m^3), V (0.017 ng/m^3), Cr (0.12 ng/m^3), Mn (0.03 ng/m^3), Co (0.05 ng/m^3), Ni (0.075 ng/m^3), Cu (0.034 ng/m^3), Zn (0.17 ng/m^3), As (0.049 ng/m^3), Se (0.06 ng/m^3), Sr (0.026 ng/m^3), Cd (0.004 ng/m^3), Ba (0.006 ng/m^3), Pb (0.1 ng/m^3), Pd (0.01 ng/m^3). The results of standard materials showed that the elements were within target recovery ratio of 100 ± 15%, which assures the accuracy of our data.

2.4. Source analysis

In the past decades, the source apportionment studies were carried out by various methods, such as the enrichment factor (Senaratne, 2004), principal component analysis (Srivastava and Jain, 2007; Thomaidis et al., 2003), scanning electron microscope (SEM) and transmission electron microscope (TEM) analysis, Chemical Mass Balance (CMB), etc (Laskin et al., 2009; Witt et al., 2010; Xie et al., 2005). The model of CMB is relatively more mature than Factor Analysis (FA, include EF and PCA) and PMF model, widely used in the source apportionment, but this model is only effective when knowing component spectrum or source profiles, otherwise the mixing of sources outputted from the model will appear unreasonable. FA model is based on the statistical correlations among the receptor component spectra, also the combination with the feature elements. This model often required a large number of FA receptor data to obtain accurate results – the greater the amount of data is, the more accurate the results are. As the samples in our study were less than 100, we didn't choose this model. PMF (Paatero, 1999; Paatero and Tapper, 1994) is an advanced source apportionment model recommended by EPA, which has been widely applied in US and Europe countries (Qin et al., 2006; Richard et al., 2011; Vassilakos et al., 2007). Compared to the CMB method, PMF doesn't require a prior assumptions of the original source profiles, and it can obtain non-