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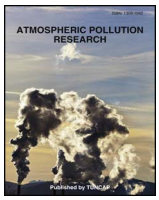

Seasonal variability and source distribution of haze particles from a continuous one-year study in Beijing

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ABSTRACT

Haze pollution by anthropogenic emitted particles is a frequent challenge for Beijing air quality in addition to the well-known dust storm events. Man-made air pollution is able to cause hazy conditions reducing the sight range. Since those air quality conditions became more and more frequent in Beijing recently, this paper focuses on the seasonal variability of the air quality during such haze episodes in relation to clear air situations. In order to find out the characteristics of airborne PM during haze episodes in different seasons as well as of the corresponding PM sources or air flow influences, a continuous one-year daily PM sampling from June 2010 till June 2011 was performed at the campus of the China University of Geoscience (Beijing). The inorganic elements, water-soluble ions, element carbon and organic carbon as well as levoglucosan, hopanes and PAHs were analyzed, respectively. Positive matrix factorization and back trajectory cluster analyses were applied and combined to identify and apportion sources. The results show that the main sources of particles during haze are secondary inorganic ions formations. Beyond that, different sources from season to season are obvious: biomass burning derived particles have high impact on summer and autumn haze, coal combustion is a major source for winter haze whereas mineral dust emissions are most prominent in spring haze. The sources of PM during clear days were dominated by mineral dust emissions and traffic. Nearby southerly industrial regions were found to be the main source areas of particles during haze in Beijing.

1. Introduction

Haze, an air pollution phenomenon, is accompanied with high airborne particulate matter (PM) mass concentrations (Zhao et al., 2013) and low visibility (Sun et al., 2006). It becomes to be an increasing focus of air quality research worldwide, thus much more attention has been paid to it (Okada et al., 2001; Chen et al., 2003; Yadav et al., 2003; Lee et al., 2006; Huang et al., 2011), especially to the most severe haze pollution event which swept most north-eastern cities of China in January 2013 (Huang et al., 2014; Ji et al., 2014; Tao et al., 2014; Wang et al., 2014; Zhang et al., 2014a, 2014b; Zheng et al., 2015). Considering that the adverse effects of PM on human health increase as PM mass concentrations increase (Ostro et al., 2006; Pope and Dockery, 2006), so finding out the sources of PM during haze become more and more important for developing effective emission reduction strategies.

Even though numerous studies of haze pollution in Beijing were done in the past (e.g. Sun et al., 2006, 2013a, 2013b; Huang et al., 2014; Zheng et al., 2015), and these studies pointed out that both of secondary inorganic ions mass concentrations and PM size increased during hazy days. The former increased to be the dominant part in PM,

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and the latter increase, from the condensation mode to the droplet mode. Additionally, the contribution from southerly direction air flow to haze was found to be significant, much higher than other directions. This is important because there are a lot of sources of air pollutants as industries and urban areas. But these study periods were not continuous, either only focusing on single haze events (e.g. Cheng et al., 2013), or only for some compound classes (e.g. Yu et al., 2013; Du et al., 2014; Gao et al., 2014). A systematic investigation of seasonal variation of characteristics and sources of particles during haze events by continuous observations is really rare.

A one-year continuous campaign in 2010/2011 is described and analyzed in this study. Haze episodes were selected on the basis of definitions which are given in the following. A chemical characterization of PM from filter samples was performed. It is from our knowledge a unique study for the time period between the Olympic Summer Games in 2008 and the huge haze in January 2013. Source apportionment was applied on the data basis of this campaign. Results of these investigations are presented and discussed, so that conclusions about possible mitigation measures to reduce or avoid haze will be given.

2. Materials and methods

2.1. Sampling strategy

From 21 June 2010 till 20 June 2011, daily PM samples (00:00–0:00 the next day, local time) were synchronously collected on 150 mm diameter quartz fiber filters (Munktell T293, Falun, Sweden) by two high volume samplers (HVS, samplers A and B, Digitel DHA-80, Hegnau, Switzerland) at the campus of the China University of Geosciences (Beijing) (CUGB, 116.35E, 39.99N, Fig. 1), which is close to the North 4th Ring Road. The measurement site was in a distance of about 20 m to a six lane road, but differentiated to this road by a 2 m high solid wall, and in about 10 m distance to the pedestrian entrance of the CUGB. The sampling heads were installed at a height of 2 m above ground, indicative for human exposure. Field blank samples of both samplers were collected every second week.

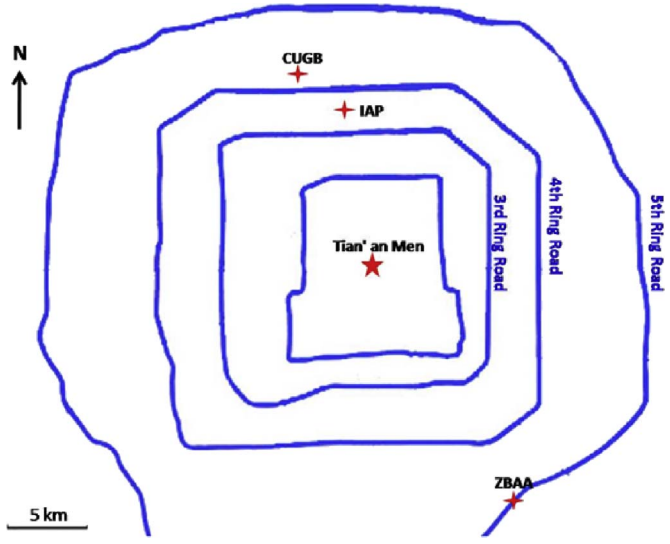

Fig. 1. The location of measurement sites in Beijing: CUGB is the China University of Geosciences (Beijing) – PM sampling; IAP is the Institute of Atmospheric Physics of the Chinese Academy of Sciences – $PM_{2.5}$ online mass concentrations, mixing layer height from ceilometer data; ZBAA is the code for the monitoring site from where one can obtain meteorological data on the website of the University of Wyoming, USA (http://weather.uwyo.edu/upperair/sounding.html).

2.2. Analytical methods

Filters of sampler A were used for the organic carbon (OC), elemental carbon (EC), water soluble ions and organic species analysis. The filters were heated at 500 °C for 6 h before sampling. Filters of sampler B were used to determine the gravimetric PM mass concentrations by an analytical balance (Mettler Analysenwaage AE240, reading precision 0.1 mg). Before weighing, 48 h equilibration of filters was performed at temperature of 22 °C ± 0.2 °C and relative humidity (RH) of 42% ± 0.5%. Inorganic elements were also analyzed from filters of sampler B.

OC and EC were analyzed by a thermal/optical carbon analyzer (DRI Model 2001A, Desert Research Institute, USA) according to the IMPROVE (Interagency Monitoring of Protected Visual Environments) A protocol in which the thermal optical reflection method (TOR) is applied (Cao et al., 2007; Chow et al., 2007).

Anions (Cl^-, NO_3^- and SO_4^{2-}) and cations (NH_4^+) were analyzed by ion chromatography (IC) (ICS-1500, Dionex, USA) and a continuous flow analyzer (CFA) ($Scan^{++}$, Skalar, The Netherlands), respectively. Punched filter parts (25 mm diameter) were extracted by 5 ml de-ionized water (Milli-Q, 18.2 MΩ cm) three times in an ultrasonic bath. Each extraction took 15 min. The extract was filtered after each extraction.

Levoglucosan, eleven hopane substances including 18α(H)-22,29,30-Trisnorneohopane (Ts), 17α(H)-22,29,30-Trisnorhopane (Tm), 17β(H)-22,29,30-Trisnorhopane (27b), 17α(H)21β(H)-30-Norhopane (29ab), 17β(H)21α(H)-30-Norhopane (29ba), 17α(H)21β(H)-Hopane (30ab), 17β(H)21α(H)-Hopane (Moretan) (30ba), 22S-17α(H)21β(H)-Homohopane (31abS), 22R-17α(H)21β(H)-Homohopane (31abR), 22S-17α(H)21β(H)-Bishomohopane (32abS), 22R-17α(H)21β(H)-Bishomohopane (32abR) and eleven PAHs including benz[a]anthracene (BAA), chrysene (CRY), sum of benzfluoranthenes (BBKF), benzo[e]pyrene (BEP), benzo[a]pyrene (BAP), perylene (PER), dibenz[a,h]anthracene (DAH), indeno[1,2,3,c,d] pyrene (IND), picene (PIC), benz[g,h,i]perylene (BGH), and coronene (COR) were measured by in situ derivatization direct thermal desorption gas chromatography time-of-flight mass spectrometry (IDTD-GC-TOFMS). Data evaluation was performed by an Agilent 6890 gas chromatograph (Agilent, USA) attached to a Pegasus III time of flight mass spectrometer (Leco, USA). More details of this method can be found in a previous study (Orasche et al., 2011).

Inorganic elements (K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, As, Sn, Sb, Ba and Pb) were analyzed by polarized energy dispersive X-ray fluorescence (PEDXRF, Epsilon 5, PANalytical, The Netherlands). The calibration was conducted by previously analyzed results from inductively coupled plasma mass spectrometry (ICP-MS). This method is described in detail by Kramar (1999).

2.3. Meteorological parameters

Temperature (T), atmospheric pressure (P), relative humidity (RH), visibility, wind speed (WS) and wind direction (WD) were obtained from the weather station ZBAA (Fig. 1, data was reported on the internet page of the University of Wyoming, USA (http://weather.uwyo.edu/upperair/sounding.html)). The available data of visibility is up to 10 km.

Mixing layer height (MLH) was determined on the basis of particle backscatter intensities by a laser-based remote sensing system, ceilometer CL31 (Vaisala GmbH, Hamburg, Germany) at the Institute of Atmospheric Physics (IAP, Fig. 1). All details about MLH determination are described in previous studies (Münkel et al., 2007; Emeis et al., 2008).

2.4. Positive matrix factorization (PMF)

PMF is thought to be a suitable tool for source apportionment, which uses a matrix of measured mass concentration and calculated uncertainties of chemical composition to produce two matrices: factor