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Chlorine levels and species in fine and size resolved atmospheric particles by X-ray absorption near-edge structure spectroscopy analysis in Beijing, China

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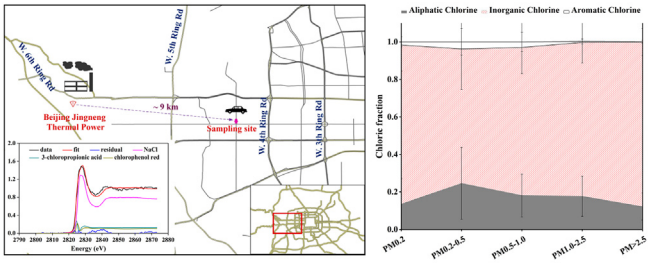
HIGHLIGHTS

- Chlorine species in size resolved atmospheric particles were measured in Beijing.
- X-ray absorption near edge structure spectroscopy was used for measurement.
- The rising trend of concentrations of atmospheric particles has been controlled.
- Inorganic chlorine was the major species of chlorine in atmospheric particles.
- High toxic aromatic chlorine presented low proportion in atmospheric particles.

GRAPHICAL ABSTRACT



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ABSTRACT

An understanding of the species of chlorine is crucial in the metropolis-Beijing, which is suffering serious haze pollution with high frequency. Particulate Matters (PMs) with five different sizes were collected in Beijing from July 2009 to March 2016, and characterized non-destructively by X-ray absorption near edge structure spectroscopy. $PM_{<0.2}$, $PM_{0.2\text{-}0.5}$ and $PM_{>2.5}$ contributed for the major PMs mass in spring and summer, $PM_{0.5\text{-}1.0}$ and $PM_{1.0\text{-}2.5}$ contributed for the major PMs mass in autumn and winter. The concentrations of the three chlorine species were in the order of inorganic chlorine (Cl_{inorg}) > aliphatic chlorine (Cl_{ali}) > aromatic chlorine (Cl_{aro}), indicating that Cl_{inorg} constituted the primary chlorine fraction and less toxic Cl_{ali} constituted the primary total organic chlorine ($Cl_{ali} + Cl_{aro}$, abbreviated as Cl_{org}) in the PMs in Beijing. In addition, these three chlorine species exhibited identical seasonal variation in $PM_{2.5}$:

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winter > autumn > spring > summer. Wet precipitation is an important factor to result in the lower mass concentrations of these three chlorine species in summer. The temporal variations of both size resolved PM mass concentrations and chlorine species concentrations suggested that the air pollution prevention and control in Beijing has just won initial success.

1. Introduction

Due to the rapid industrialization and urbanization, especially the special substantial coal-dependent energy consumption structure, the haze pollution in China, especially in Beijing, is triggering great concern to the scientific and medical communities, as well as to legislators and the public (Li et al., 2017). The haze events with low visibility have been occurring with increasing frequency and regional area since 2011 all over China. In 2013, the air pollution was classified as one of the major causes of cancer and among Group 1, or top human carcinogens by the International Agency for Research on Cancer (IARC, 2013), which is the specialized World Health Organization's cancer agency. Several epidemiological studies have unraveled that the atmospheric UFPs are an important factor of adverse health effects due to its size, surface area, chemical composition, and ability to translocate through the epithelium of terminal bronchioles and alveoli (Chen et al., 2016; Cho et al., 2009; Ramgolam et al., 2009; Traboulsi et al., 2017). Chen et al. (2013) commented that 350,000 to 500,000 people die prematurely each year in China due to the air pollution issue. In addition, it should be noted that $PM_{2.5}$ has become the fourth largest threat to the Chinese people's health (Yang et al., 2013). Therefore, the critical haze pollution has aroused great public attentions to the fine/ultra fine particles (UFPs) in the atmosphere. Furthermore, it is highly required to collect and characterize fine particulate matters (PMs) with different size levels to demonstrate their physicochemical properties and corresponding risks to human (Butler et al., 2003).

Chlorine is a primary elemental component for atmospheric PMs (Cicerone, 1981; Oberg, 2002; Oberg et al., 2005; Simpson et al., 2015), and understanding of its chemical species is very important in source identification, transportation, and health risk estimation of PMs (Angyal et al., 2011; Kertesz et al., 2013; Saitoh et al., 2008; Wonglee et al., 2011). On the one hand, many artificial and hazardous substances in environment were chlorinated, such as PCBs (Shao et al., 2016; Yang et al., 2012a), PCNs (Die et al., 2016; Liu et al., 2014), PCAs (Chaemfa et al., 2014), PCDD/Fs (Morales et al., 2014), OCPs (Shao et al., 2016; Yang et al., 2012b), DPs (Sverko et al., 2011), with characteristics of persistence, long-range transportation, bioaccumulation, and high toxicity (Lui et al., 2017). On the other hand, more than 1500 chlorinated compounds occur naturally, including, for example, alkenes, terpenes, steroids, fatty acids and glycopeptides, with low or no toxicity (Oberg, 2002). Therefore, it is of importance to differentiate the ratio of inorganic, aliphatic, and aromatic chlorine with different toxicities for the risk assessment.

To characterize all kinds of chlorinated compounds synchronously is almost impossible, owing to the chemical complexity and the typically small sample size (often no more than a few mg) of PM samples collected on filters. In addition, Xu et al. (2005) have revealed that the relative proportions of the known organic chlorine (such as HCHs, DDTs, chlordanes, PCBs) only account for 0.04–0.70% and 0.06–0.30% of the total extractable organic chlorine in $PM_{2.5}$ and PM_{10}, respectively. Therefore, the traditional combination of GC/MS, HPLC/MS, ion chromatography, and instrumental neutron activation analysis could not give comprehensive information about the chlorine contents and species, especially the proportion of aromatic chlorine with higher health risk.

X-ray absorption near-edge structure (XANES) is the region of an X-ray absorption spectra within ~50 eV of the absorption edge, which is a widely used tool to elucidate local coordination environment and chemistry of the absorbing atom (Zheng et al., 2011). The advent of dedicated synchrotron facilities, allowing the exploitation of the particular qualities of synchrotron radiation as a research tool, has made in-situ nondestructive investigation of chlorine distribution and species in environmental samples practicable (Leri et al., 2006). Up to date, there were limited reports on the species of chlorine in the atmospheric PMs in Beijing, China. Therefore, such research is highly required for the source identification of chlorine and revealing its species components for risk assessment at present.

The aim of this study is to: 1) study seasonal variation of atmospheric PM samples with five size levels ($PM_{0.2}$, $PM_{0.2\text{-}0.5}$, $PM_{0.5\text{-}1.0}$, $PM_{1.0\text{-}2.5}$ and $PM_{>2.5}$) in Beijing, China; 2) investigate their size distribution patterns of the collected PMs in haze days and non-haze days; 3) characterize concentration and species of chlorine in size resolved PMs by XANES spectroscopy for the first time; 4) study the temporal trends of chlorine and its species; 5) study their relationships among inorganic chlorine (Cl_{inorg}), aliphatic chlorine (Cl_{ali}), and aromatic chlorine (Cl_{aro}) in atmospheric PM samples in five size levels.

2. Materials and methods

2.1. Sampling

Beijing, located at 30°38′~41°05′, is in a warm temperate zone. Beijing has a distinct monsoon-influenced humid continental climate, characterized by higher humidity in summer due to the East Asian monsoon, and colder, windier, drier in winter owing to the Siberian anticyclone. The wind system of this region is at 700–800 m above sea level, which is prevailed with southeast winds in summertime, while prevailed with northwest wind in wintertime. Its precipitation distribution is uneven, with majority in summer. These meteorological and geographical characteristics along with the increasing haze events have made Beijing an ideal spot to study atmospheric PMs.

PM samples were collected at roadside with a height ~1 m above the ground (39°54′ N, 116°14′ E) from July 2009 to March 2016. Air samples were typically collected every 10 days, using a commercial DGI-1570 Dekati gravimetric impactor (Dekati Ltd., Finland) with four impaction stages and one backup filter. PM samples were collected at a calibrated airflow of 70 L min^{-1} for 24 h, therefore, a total about 101 m^3 of atmospheric particles was collected for each sample. As shown in Fig. 1, it classifies particles into five size fractions with aerodynamic cutpoints of 2.5, 1.0, 0.5, and 0.2 μm, respectively. The five size stages are as follows: < 0.2 μm; 0.2–0.5 μm; 0.5–1.0 μm; 1.0–2.5 μm; and >2.5 μm. After the four