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Identification of the typical metal particles among haze, fog, and clear episodes in the Beijing atmosphere

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HIGHLIGHTS

- Fe-rich particles (48.5%) dominate the metal particles, followed by Zn-rich particles (34.9%) and Pb-rich particles (15.6%).
- Various speciations are speculated to come from different sources, such as waste incineration, coal combustion, biomass burning.
- Fe_3C was firstly observed in the atmosphere as an indicative of steelwork according to our knowledge.
- Fog and haze episodes probably accelerate the heterogenic process of zinc oxides to form nitrate and sulfate.

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ABSTRACT

For a better understanding of metal particle morphology and behaviors in China, atmospheric aerosols were sampled in the summer of 2012 in Beijing. The single-particle analysis shows various metal-bearing speciations, dominated by oxides, sulfates and nitrates. A large fraction of particles is soluble. Sources of Fe-bearing particles are mainly steel industries and oil fuel combustion, whereas Zn- and Pb-bearing particles are primarily contributed by waste incineration, besides industrial combustion. Other trace metal particles play a minor rule, and may come from diverse origins. Mineral dust and anthropogenic source like vehicles and construction activities are of less importance to metal-rich particles. Statistics of 1173 analyzed particles show that Fe-rich particles (48.5%) dominate the metal particles, followed by Zn-rich particles (34.9%) and Pb-rich particles (15.6%). Compared with the abundances among clear, haze and fog conditions, a severe metal pollution is identified in haze and fog episodes. Particle composition and elemental correlation suggest that the haze episodes are affected by the biomass burning in the southern regions, and the fog episodes by the local emission with manifold particle speciation. Our results show the heterogeneous reaction accelerated in the fog and haze episodes indicated by more zinc nitrate or zinc sulfate instead of zinc oxide or carbonate. Such information is useful in improving our knowledge of fine airborne metal particles on their morphology, speciation, and solubility, all of which will help the government introduce certain control to alleviate metal pollution.

1. Introduction

Epidemiological studies reported that exposure to airborne particulates is linked with increased respiratory and cardiovascular disease, and increased risk for cancer or death (Dadvand et al., 2012; Janssen et al., 2013; Pope et al., 2002). Although relatively little is known about the specific chemical constituents responsible for adverse effects on human health, particle-bound metals are implicated in a number of studies (Birmili et al., 2006; Censi et al., 2011; Costa and Dreher, 1997). Emission of heavy and trace elements into the atmosphere can also affect the environment, either directly by their ecological toxicity or indirectly through geochemical accumulation that potentially can result in oral exposure through the food web (Utsunomiya et al., 2004). It is well-known that lead is a highly toxic element to the human body and that even at low concentrations, which will have severe physiological or neurological effects, particularly for children (Canfield et al., 2003; Zahran et al., 2013). The highly toxic effect of Pb is believed to be caused by its high binding affinity for thiol and phosphate groups in enzymes, proteins and cell membranes (Baltrusaitis et al., 2012). Besides the amount of particle matter (PM) ingested, several particle-related parameters, such as particle size, solubility, and morphology, and species play a crucial role in the development of adverse health effects from air pollution (Birmili et al., 2006; Chen et al., 2006; Limbach et al., 2007; Lin et al., 2005; Moffet et al., 2008). The size will influence their reactivity, toxicity, solubility and their fate in the ambient environment (Lin et al., 2005). It has been demonstrated that ultrafine particles have a significantly greater inflammatory effect

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on the lungs than the coarser fraction of the same material at the same mass level (Lin et al., 2005). Hence, researchers have paid increasing attention to nanoparticles in the atmosphere (Limbach et al., 2007; Utsunomiya et al., 2004). Since particle-bound metals need to dissolve and become free ions in the lung fluid, particle solubility is considered a major criterion for the bioavailability and therefore toxicity (Birmili et al., 2006; Costa and Dreher, 1997). Animal experiments in vivo laboratory and some human exposure studies unanimously agreed that long-term exposure to certain trace metals can result in pathogenic effects ranging from learning disabilities, development of respiratory inflammation to cancer, and damage of vital organs (Utsunomiya et al., 2004). The morphology of metal particles has also been linked with health effects in toxicology studies. If toxic trace elements are homogeneously dispersed as impurities in insoluble larger-size particles, risks to the health and environment are less than if they occur as distinct phase with high solubility in nanoscale particles (Utsunomiya et al., 2004).

Since metal-bound PM comprises a broad class of morphologically and chemically heterogeneous species, the average composition and average aerodynamic diameter obtained from bulk analyses do not describe well the population of the particles (Chen et al., 2006). The toxicity of an element is quite different because of the variation in its form of occurrence within PM. Chemical compositions of metal-bound PM can be more clearly elucidated by the application of single-particle analysis, a task that typically involves the use of a transmission electron microscope (TEM). TEM is a powerful tool to be capable of simultaneously obtaining unique information on individual particles regarding metal speciation, size, mixing state, and morphology, all of which may correlate better with potential toxicological mechanisms (Chen et al., 2006). Several studies have succeeded in identifying the particles bearing toxic elements using TEM (Adachi and Buseck, 2010; Chen et al., 2006; Gieré et al., 2006; Li and Shao, 2009a; Li et al., 2013a; Utsunomiya and Ewing, 2003; Utsunomiya et al., 2002, 2004; Zhou et al., 2014).

Rapid industrialization and urbanization in China have contributed massive quantities of anthropogenic pollutants into the atmosphere (Chameides et al., 1999). With expansion of the megacities and their surrounding area in the past two decades, severe haze and fog episodes have become more frequent, which has raised an increasing environmental concern (Chameides et al., 1999). Stagnation occurs during episodes of urban haze, when there is insufficient wind velocity to carry pollutants away from the city. Anthropogenic sources of metal-containing particles are thus enriched in the urban atmosphere (Katrinak et al., 1993). Furthermore, metal-containing aerosols continue to collide and combine during the long atmospheric residence time, which will lead to the variation in their form of occurrence within PM. Exposure to moisture and acidic gases, the particles can undergo geochemical transformations that convert metals from relatively refractory phases into phases with greater liability. Based on a simulated investigation, Baltrusaits et al. proposed that heterogeneous chemistry with NO_x can increase the mobilization of heavy metals, such as lead, in the pollutant atmosphere (Baltrusaitis et al., 2012). On the other hand, a portion of solubilized metals can reprecipitate as secondary minerals, forming rinds on particle surfaces, or hybridizing into other particles with larger sizes, which may decrease their potential bioavailability. Field observations in Mexico City have identified that metal-bearing nanoparticles were often hosted within large aerosol particles, indicating their complicated occurrences in the pollutant urban atmosphere (Adachi and Buseck, 2010). Up to date, some characteristic features of articles such as metal concentrations have been provided by a significant number of previous studies (Baltrusaitis et al., 2012; Karlsson et al., 2005). However, detailed information on metal-bound particles during haze–fog episodes is still scarce with just a few of the chemical elemental bulk analyses having been performed (Deng et al., 2011; Huang et al., 2012). Chemical compositions of metal-bearing particles should be directly identified by the application of single-particle analysis, such as TEM.

The Beijing metropolitan region is a useful area for a representative study of metal pollution during haze–fog episodes in China. In this work, we present chemical composition data from the single-particle samples using TEM-EDS. We focus in particular on typical metal elements in the aerosol samples, discussing their abundances, transports, origins, and reaction mechanisms. Backward trajectories are then employed to determine the potential source regions for these toxic metals. This field work and subsequent laboratory analyses enable the comparison of various metal-containing aerosol characteristics among clear, foggy, and hazy episodes, which may be crucial for developing cost-effective air pollution control strategies in China.

2. Experimental

2.1. Sampling

Aerosol samples were collected consecutively over the period of May 23 to Jun 24, 2012, at the Institution of Atmospheric Physics (39°58′N, 116°22′N), Beijing, China. The sampling site is located on the rooftop of a two-story building (about 8 m above the ground) in the campus. The surroundings of the sampling site consist mainly of residential dwellings. Several steel plants scatter around with the distances from 6 to 25 km. In addition, a waste incineration facility (Gaodun) locates 8 km northeast, with a capacity of 1600 t d^{-1}. Apart from these point sources, vehicle emission affects the study site as well. The North Third Ring Road is suited 360 m south and North Fourth Ring Road 380 m north. A single-stage cascade impactor with 1.0-mm-diameter jet nozzle was used to collect particles on the copper grids for TEM analysis. Sampler inlet was mounted at the height of 2 m vertically above the floor. Air flow rate was set at 1 L min^{-1}, and the sampling duration time depended on the ambient visibility, ranging from 30 s to 15 min. TSP are probably collected by the sampler. However, ultrafine particles or particles larger than 2.5 μm are scarcely detected, since the collection efficiency is highest with the particles around 0.65 μm diameter assuming the particle density to be 1.2 g cm^{-3} (Li et al., 2011a). Samples were preserved in the plastic carriers, and then sealed in a plastic bag, to minimize the exposure to the atmosphere.

Samples were grouped by meteorological conditions, that is, foggy, hazy and clear episodes. Here, we adopted the Chinese Meteorological Administration (CMA) definition for these weather situations which last longer than 3 h in this study as follows: excluding precipitation, foggy: visibility < 10 km and relative humidity (RH) > 90%; hazy: visibility < 10 km and RH < 80%; clear: visibility > 10 km. When the RH is between 80% and 90%, it depends. We attribute mist defined by the Weather Underground to the fog group. Meteorological data (Table 1) was downloaded from Weather Underground (www.wunderground.com).

2.2. TEM analysis

A JEOL-2010F field emission high-resolution transmission electron microscope (FE-HRTEM) coupled with an Oxford energy-dispersive X-ray spectrum (EDS) was applied to investigate the morphology, composition and the crystallography of the interested particles collected on the TEM copper grids. EDS analysis was performed in an exposure time of 15 s, to minimize the beam damage to sensitive particles. Identification and semi-quantification were confined to the elements heavier than carbon.

As the TEM copper grids were coated with carbon films (carbon type-B, 300-mesh copper, Tianld Co., China), Cu and C were ruled out of consideration. Selected area electron diffraction (SAED) pattern or high resolution TEM (HRTEM) images were used to examine the structure of crystalline particles. PCPDFWIN (Version 2.02) software was used to index the metal compounds by comparing the *d*-spacings of SAED pattern or HRTEM images in some interested parts of particles with the crystallographic data from the International Centre for