Chemosphere 181 (2017) 259–269

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Characterization of typical metal particles during haze episodes in Shanghai, China

Rui Li [a], Xin Yang [a], Hongbo Fu [a, b, *], Qingqing Hu [a], Liwu Zhang [a], Jianmin Chen [a, **]

[a] Shanghai Key Laboratory of Atmospheric Particle Pollution and Prevention, Department of Environmental Science & Engineering, Fudan University, Shanghai 200433, China

[b] Collaborative Innovation Center of Atmospheric Environment and Equipment Technology (CICAEET), Nanjing University of Information Science and Technology, Nanjing 210044, China

HIGHLIGHTS

- Metal-containing particles were hosted by sulfates, nitrates, and oxides.
- Six main types of Fe-containing particles could be observed by ATOFMS.
- TEM and ATOFMS can supplement one another for single particle analysis.

ARTICLE INFO

Article history:
Received 3 January 2017
Received in revised form
23 March 2017
Accepted 27 March 2017
Available online 19 April 2017

Handling Editor: R Ebinghaus

Keywords:
Trace metals
Haze
Single particle
TEM
ATOFMS

ABSTRACT

Aerosol particles were collected during three heavy haze episodes at Shanghai in the winter of 2013. Transmission electron microscopy (TEM) coupled with energy dispersive X-ray spectroscopy was used to study the morphology and speciation of typical metal particles at a single-particle level. In addition, time-of-flight aerosol mass spectrometry (ATOFMS) was applied to identify the speciation of the Fe-containing particles. TEM analysis indicated that various metal-containing particles were hosted by sulfates, nitrates, and oxides. Fe-bearing particles mainly originated from vehicle emissions and/or steel production. Pb-, Zn-, and Sb-bearing particles were mainly contributed by anthropogenic sources. Fe-bearing particles were clustered into six groups by ATOFMS: Fe-Carbon, Fe-Inorganic, Fe-Trace metal, Fe-CN, Fe-PO_3, and Fe-NO_3. ATOFMS data suggested that Fe-containing particles corresponded to different origins, including industrial activities, resuspension of dusts, and vehicle emissions. Fe-Carbon and Fe-CN particles displayed significant diurnal variation, and high levels were observed during the morning rush hours. Fe-Inorganic and Fe-Trace metal particle levels peaked at night. Furthermore, Fe-Carbon and Fe-PO_3 were mainly concentrated in the fine particles. Fe-CN, Fe-Inorganic, and Fe-Trace metal exhibited bimodal distribution. The mixing state of the particles revealed that all Fe-bearing particles tended to be mixed with sulfate and nitrate. The data presented herein is essential for elucidating the origin, evolution processes, and health effects of metal-bearing particles.

1. Introduction

Trace metals hosted by aerosols have been focused on for decades because of their significantly adverse effects on the environment and human health (Allen and Turner, 2008). With the rapid development of urbanization and industrialization, the emissions of trace metals increased sharply in recent years (Mielke and Zahran, 2012; Tian et al., 2012). Liu et al. (2015) observed that Zn, Pb, Mn, and Cu were enriched in aerosol particles in Changsha, China. Moreover, the concentrations of Pb and Zn in the dusts were 2.5 and 3.8 times higher than the background values in Shanghai, respectively (Shi et al., 2008). The trace metals present in the dusts could be lifted into the atmosphere by strong wind and human activities (Csavina et al., 2012). Moreover, these trace metals lifted into the atmosphere will be scavenged by fine particles and undergo long-range atmospheric transportation, thereby affecting the

* Corresponding author. Shanghai Key Laboratory of Atmospheric Particle Pollution and Prevention, Department of Environmental Science & Engineering, Fudan University, Shanghai 200433, China.
** Corresponding author.
E-mail addresses: fuhb@fudan.edu.cn (H. Fu), jmchen@fudan.edu.cn (J. Chen).

http://dx.doi.org/10.1016/j.chemosphere.2017.03.140
0045-6535/

ecological safety in remote alpine areas. Bing et al. (2016) reported that Pb reached moderate contamination and exerted eco-risk at Gongga Mountain. In addition to the negative effects on the environment, trace metals also play a crucial role on the human health. Aerosol particles, particularly the fine fraction, could increase one's susceptibility to respiratory diseases and reduce lung function. Moreover, some trace metals such as Pb and Hg could affect the nervous system, consequently leading to memory disturbances, anger, sleep disorders, and blurred vision (Ewan and Pamphlett, 1995; Ratnaike, 2003). It should be noted that trace metals can also affect the developing fetus. Bellinger (2005) concluded that parental lead exposure made non-negligible contributions to congenital malformations. Therefore, it is imperative to investigate the level of pollution by trace metals in aerosol particles.

A number of studies on trace metals in aerosol particles, including their concentration, size distribution, source, and potential health risk, have been conducted around the world. Liu et al. (2015) observed that Pb and Cu were mainly concentrated in fine particles, while Ni and Cr accumulated in coarse particles (Liu et al., 2015). Li et al. (2017) reported that some trace metals (e.g., Pb, Cd, Zn, Cr) displayed higher values in the haze-fog episode than on the clear days. They further concluded that these trace metals originated from anthropogenic sources by using the enrichment factor method. In addition to the enrichment factor method, isotopic tracing technology has been applied to identify the source of trace metals in recent years. Chen et al. (2008) observed that the Pb isotope ratios of particulate matter of ≤ 2.5 μm ($PM_{2.5}$) in the Baoshan steel plant fell well within the scope of coal Pb isotopic composition, indicating the contribution of coal combustion to the trace metal pollution. Borrok et al. (2010) reported that $\delta^{66}Zn$ of PM was close to that of burning of coal and tire derived fuel. Additionally, it has been confirmed that nanoparticles have greater inflammatory effects on the lungs than coarser fractions of the same material (Lin et al., 2005). In general, trace metals are inclined to accumulate in the nanoparticles and internally mix with S-rich or N-rich particles (Li et al., 2013b). Thus, the risks of ultrafine metal-bearing particles with high solubility are significantly higher than those of insoluble larger sized metal-bearing particles for human health (Utsunomiya and Ewing, 2003). To date, studies on the morphology and speciation of aerosol particles bearing trace metals are relatively scarce, which are key points to identify the source and evaluate the health risk of trace metals.

Transmission electron microscopy (TEM) is considered as a powerful tool to obtain information at an individual particle level, including size, morphology, structure, speciation, and mixing state. Hu et al. (2016) collected single particle samples in different weather conditions and further classified these particles under TEM into eight categories including C-rich, Ca-rich, mineral, S/N-rich, Fe-containing, Zn-containing, Pb-bearing, and sea salt particles. Li et al. (2013a) observed that metal-bearing sulfates are generally much more abundant than ammoniated sulfate particles during Chinese New Year. Although TEM analysis shows high spatial specificity in appearance, composition, and structure, this method is completely artificially operated and labor intensive, leading to poor statistics. In contrast, aerosol time-of-flight mass spectrometry (ATOFMS) could overcome the defects of the former because it is an excellent online instrument for good statistics despite the lack of an image. Furthermore, the size and speciation of particles could be determined at high time resolution (Zhang et al., 2009). Zhang et al. (2009) categorized Pb-bearing particles into eight main classes and thus concluded that they were possibly derived from coal combustion, waste incineration, phosphate industry, and sea salt. Wang et al. (2014) grouped urban aerosol particles of Shanghai into inorganic dust, biomass burning particles, elemental carbon, and organic carbon by ATOFMS. Smith et al. (2012) observed that ATOFMS particle types were equivalent to the TEM particle types. Thus, the combination of TEM and ATOFMS could accurately reveal the characteristics of aerosol particles.

As a result of rapid economic growth and urban development, China is suffering from serious atmospheric pollution. Serious haze and fog events have been frequently observed in many Chinese cities. The concentrations of Al, Fe, Ni, and V were enhanced during the haze episodes compared to that on clear days (Wang et al., 2015). Moreover, trace metals play crucial roles in the formation of haze episodes by catalyzing the production of secondary species, such as nitrates and sulfates (Li et al., 2010). Shanghai is an international metropolis with a population of over 20 million and is an important emission source of trace metals because of the presence of many steel makers, incinerators, and seaports (Gao et al., 2009; Zhou et al., 2009). Hence, it is essential to characterize typical metal particles to assess their effects on the formation of haze. In the present study, we focused on the morphology, abundance, and speciation of typical metal particles in haze episodes by TEM. Moreover, ATOFMS was used to probe Fe-bearing particles. The result presented herein will be beneficial to develop cost-effective atmospheric pollution control policies in China.

2. Experimental section

2.1. Sampling site description and sample collection

Aerosol particles were collected during three haze periods, namely November 7th, December 2nd, and December 12th in Shanghai, China (Table S1). The sampling site is located on the rooftop of a five-story building (approximately 20 m above the ground) in the campus of Fudan University, and no high buildings spread around within 100 m range. The sampling site is close to main roads such as Guoding Road, Guoquan Road, and Handan Road. There are many commercial streets and residential dwellings around the sampling site. National Container Processing Company and Baoshan steel factory are situated approximately 15 and 21 km north of the sampling site, respectively. Two waste incineration facilities, namely Jiangqiao and Yuqiao, are located 13 km to the west and 16 km to the south, respectively. The sampling site can be regarded as a representative urban site affected by the common effects of residential, traffic, construction, and industrial sources. Haze and fog events were distinguished according to the definition for these weather situations adopted by the Chinese Meteorological Administration. The haze event is characterized by low visibility (<10 km) and a relative humidity of <80%. Meteorological data are summarized in Table S1, which were obtained from Weather Underground website (http://data.cma.cn/).

Single particles for TEM analysis were collected directly onto 300-mesh copper TEM grids coated with carbon films using a single-stage cascade impactor. Sampling periods ranged between 30 and 300 s, depending on the particle loading in the atmosphere. The collected samples were put in plastic carriers and then stored in a desiccator to preserve them for further analysis. More detailed information about the sampling process is given in a previous work (Fu et al., 2014).

2.2. TEM analysis

The aerosol particles sampled on the TEM grids were investigated using a JEOL-2010F field emission High Resolution Transmission Electron Microscopy (HRTEM) equipped with an Oxford energy-dispersive X-ray spectrometer (EDS) to obtain the morphology and composition of particles. EDS readings were recorded in TEM image mode and then quantified using the ES Vision software that uses the thin-foil method to convert the X-ray