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Source and mixing state of iron-containing particles in Shanghai by individual particle analysis

Guohua Zhang [a,b], Xinhui Bi [a,*], Shengrong Lou [c], Lei Li [d], Hongli Wang [c], Xinming Wang [a], Zhen Zhou [d], Guoying Sheng [a], Jiamo Fu [a,d], Changhong Chen [c,*]

[a] *State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, PR China*
[b] *Graduate University of Chinese Academy of Sciences, Beijing 100049, PR China*
[c] *Shanghai Academy of Environmental Sciences, Shanghai 200233, PR China*
[d] *School of Environmental and Chemical Engineering, Shanghai University, Shanghai 200444, PR China*

HIGHLIGHTS

- Number fraction of Fe-containing particles varied from <1% to 15%.
- Fe-containing particles in Shanghai most correspond to anthropogenic sources.
- Dust is suspected to be more responsible for the spike of Fe-containing particles.
- Anthropogenic Fe aerosol tended to associate with secondary species.

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ABSTRACT

Bioavailable iron (Fe) is an essential nutrient that can control oceanic productivity, thereby impacting the global carbon budget and climate. Therefore it is of vital importance to identify chemical species and mixing state of Fe-containing particles in the air, which are demonstrated to pose substantial impact on bioavailability of Fe. Using a single particle aerosol mass spectrometer (SPAMS), ~2 000 000 individual particles with mass spectra were collected in Shanghai for nearly 22 d during the winter of 2011. Number fraction of Fe-containing particles (Nf_{Fe}) varied in a wide range (<1–15%) throughout the measurement. Fe-containing particles were mainly clustered into four chemical groups, comprising of Fe-rich, K-rich, Dust and V-containing particle types. Analysis of mass spectra and mixing state suggests that Fe-containing particles correspond to various sources in Shanghai, especially anthropogenic sources iron/steel industrial activities, and fly ashes from both biomass burning and coal combustion, accounting for ~55% and ~18%, respectively. However, invasion of dust from northern desert areas is suspected to be more responsible for the spikes of Nf_{Fe} (>10%), when Dust particle type contributed to >50% of Fe-containing particles. It is also revealed that Fe-containing particles were internally mixed with secondary species (e.g., sulfate and nitrate). Anthropogenic K-rich and Fe-rich particles tended to associate with both sulfate and nitrate, and thus might lead to more fraction of soluble Fe, compared to Dust particles. These results imply that atmospheric processing of Fe-containing particles from various sources might vary and thus would change the bioavailability of atmospheric Fe.

1. Introduction

As the dominant species of the transition metals in the atmosphere, iron (Fe) substantially impacts human health, atmospheric physics and chemistry, and bioavailability to marine ecosystem (Prahalad et al., 2001). Atmospheric Fe associates with adverse health effects due to mechanisms such as DNA strand breakage and tissue or cell damage (See et al., 2007). Fe influences on the optical property of mineral dust (Moosmüller et al., 2012), and also is involved in the atmospheric conversion of S(IV) to S(VI), a substantial pathway for global atmospheric sulfate production (Alexander et al., 2009). Furthermore, atmo-

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* Corresponding authors. Tel.: +86 20 85290195; fax: +86 20 85290288 (X. Bi), tel.: +86 21 64085119; fax: +86 21 54641938 (C. Chen).
E-mail addresses: bixh@gig.ac.cn (X. Bi), chench@saes.sh.cn (C. Chen).

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spheric Fe plays an important role in the global carbon cycle through effects on marine productivity that is expected to have feedback effects on climate and dust production (Mahowald et al., 2005).

Aerosol Fe solubility varies in a wide range and therefore it represents the major uncertainty in its impacts as aforementioned (Mahowald et al., 2009). It had been reported that Fe solubility from various sources is diverse, spanning four orders of magnitude (Schroth et al., 2009). The soluble fraction of Fe in Chinese desert soil was ~0.4 ± 0.3% (Zhuang et al., 1992), however, aerosol Fe solubility heterogeneously distributes in space and time (0.001–80%) (Mahowald et al., 2005; Ooki et al., 2009). Natural emissions represent the predominant sources of atmospheric Fe, accounting for 70–80% (Jickells et al., 2005). However, recent studies highlight the important role of industrial activities, coal combustion and biomass burning in the increased soluble aerosol Fe (Guieu et al., 2005; Chen et al., 2012). Although combustion sources are not important for the total Fe mass compared to natural sources, they can contribute up to 50% of soluble Fe deposited into oceanic regions (Luo et al., 2008).

A variety of atmospheric processes, including photochemistry, organic complexion, and in particular cloud processing, can influence aerosol Fe speciation and its solubility. It had been well-documented that aerosol acidification involving urban pollutants plays a substantial role in the increase of soluble Fe (Rubasinghege et al., 2010). Many studies attempted to investigate the correlation between aerosol Fe fractional solubility and concentrations of acid species (Hand et al., 2004; Baker et al., 2006), in order to interpret a potential link between acid processing and Fe solubility. However, Baker and Croot (2010) emphasized the conformation of physical contact between Fe and acidic compounds on the exactly same particles, even if acid processing is the primary atmospheric control of the Fe fractional solubility. Aerosol Fe mixing state, referring to the association of Fe with various species such as sulfate, organics and nitrate, is the net result of primary emissions as well as subsequent atmospheric chemical and physical processes, and thus it represents one of the most controlling factors that affect aerosol Fe solubility (Baker and Croot, 2010; Chen et al., 2012). Therefore, knowledge on the sources and mixing state of aerosol Fe is a necessity and it helps to understand the effect of aerosol Fe on the marine productivity and global climate change.

Located near the East China Sea, Shanghai develops with many industries, such as Iron & Steel and petrochemical complex, which might be associated with frequently observed high aerosol loadings (Fu et al., 2008). Single particle mass spectrometer has been applied to study the sources and the formation mechanisms of aerosols in the atmosphere of Shanghai (e.g., Zhang et al., 2009). Using the similar technique, Furutani et al. (2011) found the importance of coal combustion source to the strength of Fe aerosols in China mainland. To date, only a few studies have focused on aerosol Fe in Shanghai (Wang et al., 2006, 2013), despite of their substantial impact on not only the air quality of Shanghai, but also the productivity of nearby waters (e.g., the Yellow sea).

In this study, a single particle aerosol mass spectrometer (SPAMS) was employed during the winter of 2011 in urban Shanghai to determine both the size and chemical composition of individual atmospheric particles, with vacuum aerodynamic diameter (d_{va}) in the size range of 0.2–2 μm. Air masses originating from the northern desert region arriving Shanghai during the winter provided an opportunity to directly observe the mixing of Fe-containing particles from both anthropogenic and natural sources with anthropogenic pollutants. A large set of single particle mass spectra was collected and analyzed in order to identify the origin and mixing state of Fe-containing particles.

2. Experiment setup

2.1. Atmospheric observations

Ambient aerosol measurement was conducted in Shanghai Academy of Environmental Sciences (SAESs), located in the center of urban Shanghai, between 9th and 31st December 2011 using a SPAMS, manufactured by Hexin Analytical Instrument Co., Ltd. (Guangzhou, China). The sampling site location with a detailed map of Shanghai industrial area, and a wind-rose for the entire measurement period are presented in Fig. S1 in Supplementary material (SM). The inlet of the sampling tube was set at 2 m above the roof of the Atmospheric Environment Monitoring Building of SAES. Local meteorological parameters, including ambient temperature (*T*, °C), relative humidity (RH, %), and wind speed (WS, $\mathrm{m\ s^{-1}}$), were available from Weather Underground (http://www.wunderground.com/), and temporal profiles of these parameters are shown in Fig. S2. Ambient *T*, RH, and WS during the field study varied between −2 and 13 °C, 25–100%, and 0–9 $\mathrm{m\ s^{-1}}$, with average values of 5.5 °C, 63%, and 3.8 $\mathrm{m\ s^{-1}}$, respectively.

Single particles detection method was described in detail in the SM. Regarding the strong dependence of particle detection efficiency on particle size and chemical components by SPAMS (Su et al., 2004), the particle counts and number fraction applied in this study only provided an indication of their relative abundance, rather than the absolute concentration.

2.2. Screening and clustering of Fe-containing particles

During the winter sampling period, a total of approximate 2 000 000 particles, with d_{va} between 0.2 and 2.0 μm, were chemically analyzed with positive and negative ion mass spectra. Fe-containing particles commonly produce an intense ion peak at mass-to-charge ratio (*m*/*z*) 56 in the positive ion mass spectrum. However, simply using ion peak at *m*/*z* 56 as a unique marker for Fe is not suitable, since it might be also generated in the form of CaO^+, KOH^+, and $C_3H_4O^+$ from other components. Therefore, the natural isotopic composition of Fe (^{54}Fe) was selected for the Fe screening process to minimize the interference from other species. The isotopic ratio of Fe ($^{56}Fe/^{54}Fe = 16$) was commonly used as a marker for Fe, although it is set relatively flexible, such as Peak-Area ratio $^{56}Fe/^{54}Fe > 3$ in Furutani et al. (2011), due to the variation of the ratio resulted from the matrix effect of laser desorption/ionization (Allen et al., 2000). In this study, all the possible Fe particles, referring to the particles contained both peaks from ^{56}Fe and ^{54}Fe, were separated into two fractions: particles with Peak-Area ratio $^{56}Fe/^{54}Fe > 10$ and <10, respectively. Indeed, the average mass spectrum of the particles with $^{56}Fe/^{54}Fe < 10$ resembled that of organic carbon, characterized by the obvious organic peaks at *m*/*z* 27$[C_2H_3]^+$, 29$[C_2H_5]^+$, 43$[C_2H_3O]^+$, 51$[C_4H_3]^+$, 63$[C_5H_3]^+$, 77$[C_6H_5]^+$ and 91$[C_7H_7]^+$ (Dall'Osto and Harrison, 2012). Therefore, Peak-Area ratio $^{56}Fe/^{54}Fe > 10$ was finally applied to strengthen the screening through excluding more ambiguous selection.

The screened Fe-containing particles were subsequently analyzed using an adaptive resonance theory based neural network algorithm (ART-2a) (Song et al., 1999), with a vigilance factor of 0.8, learning rate of 0.05, and 20 iterations. The chemical compositions of the produced clusters resulted from ART-2a were carefully examined to identify whether these clusters corresponded to the assignment of Fe. A few clusters characterized by relative high OC peaks (*m*/*z* 27, 37, 43) and low intensity at *m*/*z* 56, representing less than 5% of the total screened particles, were not likely to be the Fe-containing particle types. Therefore, they were excluded from the screened Fe-containing particles to avoid the ambiguous assignment.