Source identification of individual $PM_{2.5}$ particles in Shanghai air in the winter of 2007 with synchrotron X-ray fluorescence microprobe*

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Abstract In order to further understand the sources of $PM_{2.5}$ in Shanghai air, the synchrotron X-ray fluorescence microprobe at the BL-4A Beamline of Photon Factory of High Energy Accelerator Research Organization, Japan, was applied to analyze the individual $PM_{2.5}$ particles collected from Shanghai air in the winter of 2007. Eight categories of emission sources were recognized in these individual particles. The source identification shows that most of the analyzed $PM_{2.5}$ particles are derived from vehicle exhaust and metallurgical emissions. This suggests that the important emission sources of $PM_{2.5}$ in Shanghai air would be vehicle exhaust and metallurgical activities.

Key words synchrotron X-ray fluorescence microprobe, $PM_{2.5}$, individual particle analysis

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1 Introduction

Fine particulate matter ($PM_{2.5}$, particulate matter with aerodynamic diameter equal to or less than 2.5 μm) represents the main mass fraction of inhalable particulate matter (PM_{10}, particulate matter with aerodynamic diameter equal to or less than 10 μm), which accounts for ∼60% of PM_{10} mass. The $PM_{2.5}$ has long residence time in the atmosphere and can penetrate deeply into the lungs; thus, the toxicity of the fine particulate matter is higher than that of coarse airborne particles. Airborne particles of fine dimensions are recognized to have a strong impact on the environment and to be of concern in health-related effects. In urban areas, the $PM_{2.5}$ pollution is of particular interest for the possible delayed health effects associated with the continuous exposure of a high-density population[1, 2]. Epidemiological studies have found an association between the concentrations of $PM_{2.5}$ and the adverse health effects[3]. Therefore, much attention has been paid to the $PM_{2.5}$ pollution.

Shanghai is the largest commercial and industrial city in China with about 19 million people distributed over 5800 km^2. It has a strong industrial base with China's largest steel plant and other major industries. At present, $PM_{2.5}$ pollution is severe in Shanghai. Annual mean concentration of $PM_{2.5}$ was 63 μg m^{-3} in Shanghai from 1999 to 2003[4]. However, recent investigations indicated that the annual mean concentration of $PM_{2.5}$ in Shanghai significantly increased, which was 94.6 μg m^{-3} from 2003 to 2005[5]. The annual means consumedly exceed the annual standard of US air quality for $PM_{2.5}$ (15 μg·m^{-3}). Some characteristics of $PM_{2.5}$ in Shanghai air have been studied in detail, including seasonal variations, compositions[4] and ion chemistry[5]. However, the understanding about sources of $PM_{2.5}$ in Shanghai is not satisfatory at present. Yue et al studied the sources of individual $PM_{2.5}$ particles collected from Shanghai in the winter of 2004 using the synchrotron X-ray fluorescence microprobe (μ-SXRF) at the Beijing Synchrotron Radiation Facility (BSRF)[6].

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About 37% of the measured $PM_{2.5}$ particles, however, were not identified by the pattern recognition (PR) system in Yue's work. This may be attributed to the large spot size of the μ-SXRF at BSRF, which was a square of 20 μm×20 μm. The spot was so large that some $PM_{2.5}$ particles could not be effectively excited in measurements of μ-SXRF. Another possible cause about the unidentified $PM_{2.5}$ particles may be the absence of fingerprint spectra of some emission sources of $PM_{2.5}$ in the fingerprint database of the pattern recognition (PR) system.

In order to further understand the sources of $PM_{2.5}$ in Shanghai air, the μ-SXRF at the BL-4A Beamline of Photon Factory (PF) of High Energy Accelerator Research Organization, Japan, was applied to analyze the individual $PM_{2.5}$ particles collected from Shanghai air in the winter of 2007. The spot size of this μ-SXRF is a square of 5 μm×5 μm, which is much better than that at BSRF. In addition, some fingerprint spectra of new emission sources of $PM_{2.5}$ were added into the PR system to improve its recognition ability in this work.

2 Experiment

2.1 Sample collection

The $PM_{2.5}$ samples were collected from 4 monitoring sites in Shanghai (Fig. 1). The sampling sites were Ren-Min-Guang-Chang (RMGC), Pu-Tuo (PT), Gang-Yan-Suo (GYS) and Yingyong-Wuli-Suo (YWS). RMGC site was located at the center of Shanghai City, which was characterized by heavy traffic and large population. PT site was located at inhabited area in the city zone. GYS site was located in the steel-industry area in the north of the city, where there are some large steel plants, including the largest metallurgic complex, the Baosteel Group, in China. YWS site was located in the Northwest suburbs of the city, about 30 km far from the center of the city. Medium volume $PM_{2.5}$ samplers (PM-2 type, made in China) were used for the sampling of $PM_{2.5}$ particulate matter. The samplers were placed on rooftops at a height of approximately 15 m. $PM_{2.5}$ particulate matter was collected on polytetrafluoroethylene filters (ϕ = 90 mm, pore size: 0.45 μm), which have low blank concentrations for determination of trace elements. The sampling at four sites was simultaneously carried out in the winter of 2007.

In order to establish a fingerprint database of emission sources, possible emission sources were sampled. These sources were metallurgic emissions (including the converter for steelmaking, the electric furnace for steelmaking, the coke oven and the sintering plant), coal combustion (including the coal-fired power plants and the coal-fired boilers), cement dust, soil dust and vehicle exhaust (including the combustion of unleaded gasoline and combustion of leaded gasoline). The preparation of targets for individual particles analysis has been detailedly described elsewhere[7].

Fig. 1. Map of sampling sites in Shanghai: A-RMGC, B-PT, C-GYS, D-YWS.

2.2 μ-SXRF analysis

Traditional source apportionment methods for air pollutants, i.e. chemical mass balance receptor model (CMB) and principal components analysis (PCA), play an important role in atmospheric environment science. The calculation of CMB and PCA is based on bulk chemical analysis of particulate matter. Individual particle analysis is a useful tool for identifying the origins of airborne particles. It can provide information concerning the origin, formation, transport, reactivity, transformation reactions and impact on the environment of the particles, which would be impossible to obtain from bulk analysis. In the past fifteen years, micro-proton induced X-ray emission (μ-PIXE) and synchrotron X-ray fluorescence microprobe were successfully applied to the individual particle analysis. In this work, individual particle analysis was applied to identify the sources of $PM_{2.5}$ particles.

Individual $PM_{2.5}$ particles were analyzed by using the μ-SXRF at BL-4A Beamline of PF of High Energy Accelerator Research Organization, Japan. A schematic diagram of the μ-SXRF is shown in

Fig. 2. The electron energy and ring current of the synchrotron light source were 2.5 GeV and 310 — 430 mA, respectively. It provides a double crystal monochromator with a crystal pair [Si(111), Si(111)] for high-energy resolution applications and a multilayer monochromator with a multilayer pair (W/B_4C) for high-flux applications. The W/B_4C multilayer monochromator was utilized in this work. Continuous synchrotron X-rays were monochromatized with the multilayer monochromator. 17.4 keV monochromatic X-ray beam was used to excite samples for determination of trace elements in the fine particles. Focusing of the monochromatic X-ray beam was performed by a Kirkpatric-Baez optics (K-B mirror), offering a square spot of 5 μm×5 μm. The photon flux of the 17.4 keV monochromatic X-ray microbeam at the sample position was about 5×10^9 ph/s/300 mA under the beam size. In order to make optimal use of the polarization, a Si(Li) semiconductor detector was mounted in the orbital plane perpendicular to the incoming beam. The detail of the μ-SXRF has been described elsewhere[8].

The sample frame was mounted on a computer-controlled XY-sample stage, in order to perform sample movements relative to the incoming X-ray beam. The determination of the measurement positions was performed with an optical microscope focusing on the irradiated surface of the sample. The microscope is connected to a CCD camera and can be operated in reflected and transmitted light mode for optical control of the measurements. The spot analysis mode was used for all presented measurements. Because high photon fluxes for excitation of samples, 60s irradiation was only needed to measure each of the individual $PM_{2.5}$ particles in this work. The individual particles on target-films were randomly chosen for measurement in the experiment.

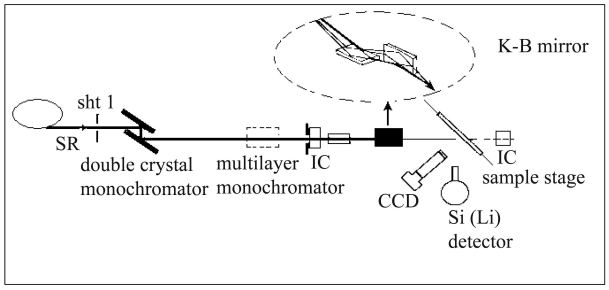

Fig. 2. A schematic diagram of the μ-SXRF at the BL-4A Beamline of PF, Japan. Either a double crystal monochromator or a synthetic multilayer monochromator was used as the monochromator.

2.3 Approach of the source identification

Previous study has revealed that individual airborne particles from different emission sources have different elemental compositions, which can be characterized by their characteristic X-ray spectra[9, 10]. Thus, patterns of the characteristic X-ray spectra are considered the chemical fingerprints of the individual particles. In the light of this view, the sources of individual particles can be identified by directly comparing the spectra of unknown individual particles with those of individual particles from the emission sources. In our earlier study, a PR system has been developed to direct recognized sources of the individual airborne particles using their characteristic X-ray spectra[11, 12].

The identification approach is as follows. Firstly, the individual $PM_{2.5}$ particles collected from the emission sources are analyzed by μ-SXRF one by one. Their spectra are recorded into a database as the fingerprint library of the emission sources in the PR system. Secondly, the individual $PM_{2.5}$ particles collected from the environmental monitoring sites are analyzed in the same facilities. The spectra are recorded in another database in the PR system. Finally, the μ-SXRF spectra of the environmental monitoring samples are compared with those in the fingerprint library of emission sources by the PR system. Sources of the individual $PM_{2.5}$ particles from the environmental monitoring site are directly identified.

As mentioned above, source identification of airborne particles is performed by the comparison of μ-SXRF spectra of unknown individual particles with those of individual particles from emission sources. The primary assumption behind the comparison method is that the individual airborne particles from different emission sources have different elemental compositions. If some of the individual airborne particles from different emission sources have the same elemental composition, the comparison method will fail. Fortunately, earlier studies (Refs. [9—11]) and this work have shown that individual airborne particles from different emission sources have different elemental compositions.

3 Results and discussion

Two hundred individual $PM_{2.5}$ particles from nine emission sources in Shanghai were analyzed by the μ-SXRF. Eight hundred individual $PM_{2.5}$ particles from four environmental monitoring sites were analyzed by the μ-SXRF also. With the PR system, the sources of

individual $PM_{2.5}$ particles were identified. Eight categories of emission sources were recognized in these individual particles. They are the vehicle exhaust from combustion of unleaded gasoline, the converter for steelmaking, the electric furnace for steelmaking, the coke oven, the sintering plant, the coal-fired power plants, the coal-fired boilers and the soil dust (Fig. 3).

The results show that the contributions of vehicle exhaust from combustion of unleaded gasoline at the four monitoring sites are the highest. They range from 47% to 60%. This may be attributed to very heavy traffic in Shanghai. There are over 2 million motor vehicles in Shanghai City. The annual consumption of gasoline was about 6.2 milliontons in Shanghai in 2006. The number of automobiles fleetly increased in recent years in Shanghai. The contribution of vehicle exhaust in the winter of 2007 was significantly higher than that in the winter of 2004 in Shanghai Ref. [6]. This suggests that the $PM_{2.5}$ pollution derived from vehicle exhaust is becoming more and more serious with the rapid increase of automobiles in Shanghai.

The contributions of metallurgical activities are the second highest at RMGC, PT and GYS (Fig. 3). They are 35%, 45% and 30% at RMGC, PT and GYS, respectively (sum of emissions from converter for steelmaking, electric furnace for steelmaking, coke oven and sintering plant). The high contributions of metallurgical activities suggest that the emission from metallurgic activities would be the main source of $PM_{2.5}$ pollution in Shanghai. This may be attributed to steel industry of Shanghai because some large steel plants, including the largest metallurgic complex in China, the Baosteel Group, are located to the North of Shanghai. The Shanghai city government has realized the pollution caused by metallurgic activities, and some effective methods have been taken to reduce the emissions of some metallurgic factories. The air quality has been improved to some extent, as demonstrated in the annual output of the industrial dust decreased from 26.9 thousandtons in 2000 to 15.0 thousandtons in 2002[13]. But further improvement of the air quality is requisite. Thus, the understanding of the pollution sources would be helpful to further improve the air quality of Shanghai. In this investigation, it is found that the contributions of the converter for steelmaking, 23% at RMGC, 38% at PT and 21% at GYS, are much more than the contributions of the electric furnace for steelmaking, the coke oven and the sintering plant (Fig. 3). If the emissions of the converter for steelmaking are controlled, the air quality of Shanghai may be improved further.

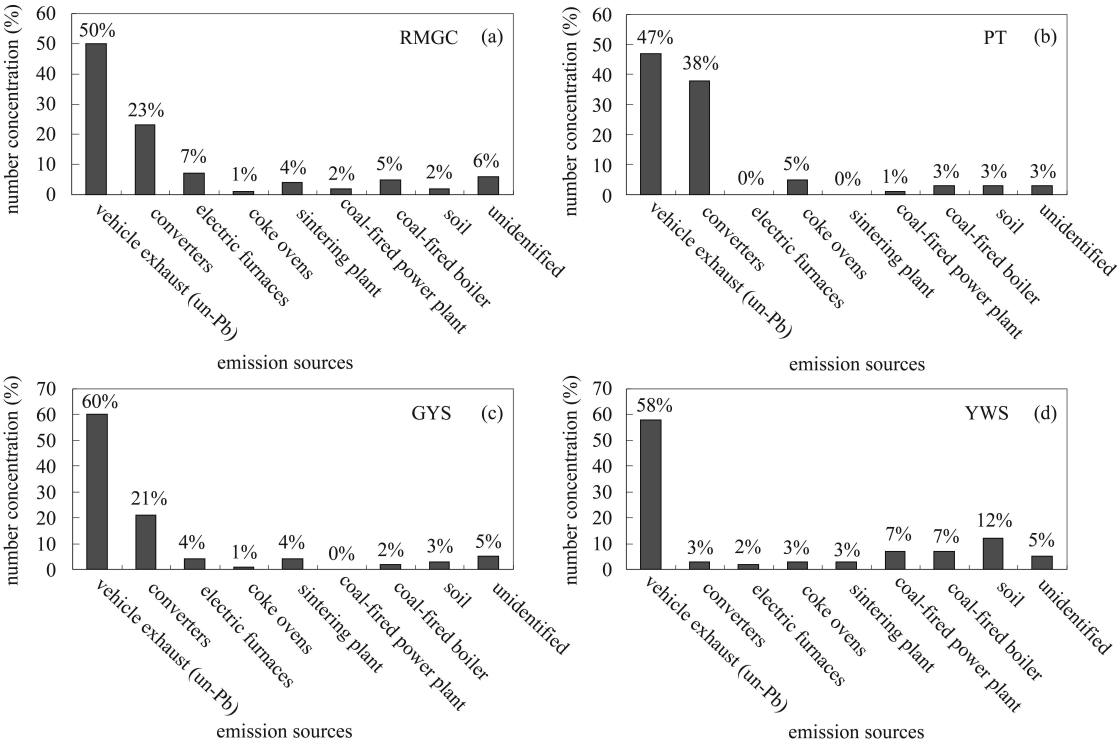

Fig. 3. Sources apportionment of analyzed $PM_{2.5}$ particles collected from Shanghai air in the winter of 2007.

Generally, it is difficult to identify similar emission by the source apportionment methods based on bulk analyses, for example, the emissions from the coal-fired power plant and the coal-fired boiler, because their major and minor compositions are similar. However, the similar emission sources can be easily identified by the individual particle analysis. In this work, the emissions from the coal-fired power plant and the coal-fired boiler were identified. It is found that the contributions of the coal-fired power plant are low, which are 2%, 1%, 0% and 7% at RMGC, PT, GYS and YWS, respectively. Also, the emissions of coal-fired boiler are low at the four monitoring sites. Therefore, the coal combustion may not be an important emission source of $PM_{2.5}$ in Shanghai. But, the study of PM_{10} sources in Shanghai shows that the contribution of coal combustion is about 12%, which can not be ignored[7]. The particles derived from coal combustion may have large particle size.

The soil dust and cement dust in a city are often caused from uncovered ground surfaces, municipal construction sites and building construction sites. Yue et al studied the sources of $PM_{2.5}$ in Shanghai air in the winter of 2004[6]. They found that the contributions of soil dust to $PM_{2.5}$ were 13% at RMGC and GYS, respectively, indicating that the emission of soil dust is not neglected. In this study, the contributions of soil dust are under 4% except the YWS site and no cement particles were detected. These suggest that the cement particles are removed from Shanghai air and that the emission of soil dust can be neglected in Shanghai. These may be attributed to the tree and grass planting on a large scale, and the setting of dustproof enclosures at the construction sites in recent years in Shanghai. The contribution of soil dust is 12% at YWS, which is higher than other monitoring sites. YWS site is located in a rural area in the suburbs of Shanghai, about 30 km away from the center of the city. Bare farmland is around YWS in winter. The higher emission of soil dust at YWS may be due to the bare farmland around it.

4 Conclusion

The synchrotron X-ray fluorescence microprobe was successfully applied to the analysis of individual $PM_{2.5}$ particles collected from Shanghai air. Eight categories of emission sources were recognized in these individual particles, which are the vehicle exhaust from combustion of unleaded gasoline, the converter for steelmaking, the electric furnace for steelmaking, the coke oven, the sintering plant, the coal-fired power plants, the coal-fired boilers and the soil dust. The source identification shows that most of the analyzed $PM_{2.5}$ particles are derived from the vehicle exhaust and metallurgic emissions. This suggests that the emissions from vehicle exhaust and metallurgical activities would be the main pollution sources of $PM_{2.5}$ in Shanghai.

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