Characterization of PM10 and PM2.5 Particulate Matter Collected in Winter Season of Shanghai City by PIXE

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ABSTRACT

The samples of PM2.5 and PM10 inhalable particulate matter had been collected during the period of December 2001-January 2002 at nineteen representative sites of Shanghai urban and suburb area in order to investigate the chemical characterization of aerosol particle in winter. The samples were analyzed to determine the average concentrations for up to twenty elements by means of the Particle Induced X-ray Emission (PIXE). It is found that the average elemental concentrations in the urban center are higher than those in the suburb, except for Ti and P. The particulate mass data demonstrate that the ratio range of PM2.5 / PM10 is from 0.32 to 0.85 and its average ratio is 0.6. The result of enrichment factor shows that the inhalable particles may be divided into two categories, i.e. soil elements from earth crust and anthropogenic pollution elements. It is noticed that the toxic or harmful elements such as S, As, Pb, Ni, Mn and Se are mainly enriched in fine particles with diameter less than 2.5µm. The fingerprints of major pollution sources such as coal (or oil) burning, vehicle exhaust emission and industry are also presented and discussed.

Keywords: PM2.5, PM10, atmospheric particulate matter, elemental concentration, PIXE, enrichment factor

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1. INTRODUCTION

For the assessment of local air pollution, besides SO₂, NO₂, O₃, the total mass of the particulate matter and its elemental composition are a very important aspect [1,]. As reported, fine particles (≤ 2.5µm) are very harmful for human health, because they penetrate and remain in the deepest passage of the lung. The long term adverse health effects lead to chronic respiratory illness, cancer, so far as to premature death [2]. Shanghai is a great industrial and commercial city in China. It has high dense residential and a very high volume of vehicular traffic. Moreover, as industrial development and energy use grow, air pollution levels begin to rise rapidly. Many industries, including power plants, refineries, chemical and steel factories are located in its suburb. Then urban air pollution becomes a serious public health concern and government has paid even more comprehensive attention to the environmental biosphere.

2 EXPERIMENTAL METHOD

2.1 Sampling

Two types of samplers provided by Rupprecht & Patashnick Co. (USA) were used for this campaign. One is a TEOM 1400 with a flow rate of 15.6 L/min, the inhalable fractions under 10µm aerodynamic diameter were collected. Another is a mini-partisol model 2100 air sampler with a flow rate of 5 L/min, the airborne particles both of coarse and fine were collected, depending on size selective inlets. In all cases, the samples of PM10 and PM2.5 were collected on Millipore cellulose ester filters (47 mm diameter, 0.45µm pore size). A period between autumn and winter was chosen because it usually exhibits the highest concentration of pollutants in one year. Each sample of 24 hours simultaneous sampling had been carried out between December 2001 and January 2002.
2.2 Analytical techniques

The elemental analysis of aerosol samples was performed by means of PIXE technique at the nuclear analysis center, Shanghai Institute of Nuclear Research [3]. PIXE spectra were fitted using AXIL software package [4] and elemental net peak area was obtained. A set of Micromatter standard reference samples (Micromatter Co, USA) was used for the quantitative calibration of the system. A check of the calibration was made by analyzing the GBW-07404 soil standard reference material prepared in China and CRM-08 vehicle exhaust standard material provided by NIES, Japan. Detection limits were about 10 ng/m³ for elements from P to V and less than 1 ng/m³ for elements from Cr to Pb. The following elements were detected: Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Rb, Sr and Pb. No significant contamination was detected in the analysis of blank filters.

3. RESULTS AND DISCUSSION

3.1 Mass Concentrations

The airborne fraction masses of PM2.5 and PM10 samples had been measured by the use of a Sartorius microbalance. The membranes were weighed under controlled conditions of humidity and temperature before and after collection of particulate matters. The highest daily PM2.5 mass concentrations are 0.226 and 0.227 mg/m³ respectively, at site of commercial district in south west of the urban and site of industrial district in south west of the suburb. Meanwhile, the highest daily PM10 mass concentrations are 0.347 and 0.389 mg/m³, respectively, at site of city center and site in north east of suburb. In contrast, the lowest daily concentrations are 0.033 mg/m³ and 0.074 mg/m³. The mass data also reveal that the mean ratio of PM2.5/PM10 accounted for 0.69 ± 0.15 and 0.52 ± 0.13 in urban and suburb, respectively. At same circulation, PM2.5 particle mass in urban is 30% higher than that in suburb. This means that the PM2.5, PM10 and PM2.5/PM10 ratios of all sampling sites in Shanghai significantly fluctuate from site to site during the wintertime. As we know, PM2.5 fine fractions maybe penetrate nostril and remain in the deepest passage of the lung. So, the fine particles pose a greater health risk than the same mass of coarse particles.

3.2 Elemental Concentrations

The analytical results demonstrate that the average elemental concentrations in the urban center are 1.3～1.8 times of those in the suburb for most elements. However, the concentrations of Ti and P in the urban are lower than those in the suburb. This is mainly due to the burning rice straw after autumn harvest by farmers as a traditional way of fertilizing, and leading to the increase of N, P, K and Ti. The related research indicates that except C, H, N, O, some trace elements such as Cr, As, Cd, Mn and Pb are also contained in the coal and oil [5]. When burning, a large quantity of SO₂ and harmful heavy metal elements are exhausted into atmosphere. Furthermore, with the carrying out of municipal engineering including construction, tunnel, building highway and bridge, more particulate matters are exhausted into ambient directly or indirectly and caused a more serious contamination for city air quality. So, motor vehicle exhaust, coal or oil fuel combustion, construction and refine industry are major sources of particulate pollution in winter of Shanghai. The results show that atmosphere pollution in urban is more serious than in suburb.

3.3 Enrichment Factor

The separation of natural and anthropogenic components is a basic task of aerosol measurements. An enrichment factor (EF) analysis is conventionally used for separating soil derived and anthropogenic components. In this research, Fe is used as reference element and the data of elemental abundance in the
crust are taken from literature [6]. Both of fig.1 and fig.2 show that the EF parameters of eight elements present a high value. They are S, Cl, Cu, Zn, As, Se, Br and Pb, respectively. It is clearly indicated that these elements are treated as anthropogenic contributions respect to crust. From different anthropogenic components, the harmful elements are exhausted into ambient atmosphere by means of combustion and transportation. Among them, S is an indicator for residual fuel burning, fine fraction Cl is an excellent indicator for power plant and refinery, Cu, Zn and Pb are often observed to be linked with traffic and smelter, As and Br are a tracer for coal or oil burning. Some elements of low enrichment factors (EF < 10 = including Si, P, K, Ca, Ti, V, Cr, Mn, Ni, Rb and Sr clearly represents soil dust aerosol particles.

4. CONCLUSIONS

PIXE results demonstrate that the concentrations of most elements are higher in the urban site than in the suburb site, except Ti and P. The most important sources of air pollution in urban are dust-soil and emission from coal or oil combustion, followed by the contributions from motor vehicle, industry emission and refuse incineration. A comparison of concentrations in aerosol and crust samples provides a tool for determining enrichment factors and for the separation of no crust components. EF analysis results show that the airborne particles of Shanghai city are divided into two kinds of sources, i.e. originating from soil dust including Si, P, K, Ca, Ti, V, Cr, Mn, Ni, Rb, Sr and originating from anthropogenic contribution including S, Cl, Cu, Zn, As, Se, Br, Pb. It is clearly demonstrated that the elements are enriched more in fine particles than in coarse particles. It is found that the harmful or toxic elements (S, As, Pb, Ni, Mn) are mainly enriched in the fine particles with the dimension less than 2.5 \( \mu m \), being easily inhaled by human. From the view of health effect, recent studies suggest that fine particles pose a greater health risk than the same mass of coarse particles.

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