V. 4. PIXE Analysis of Atmospheric Aerosols from Asian Continent

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Introduction

A large amount of yellow sand dust particles is transported from Asian continent, especially in spring season. It is known as the Kosa. Yellow sand dust is common interest for North East Asia including Japan, China and Korea, as these particles sometimes affect traffic, climate and human health. Yellow sand dust is known as a natural phenomenon, but is considered as an environmental problem, as these particles are mixed with anthropogenic aerosols over the industrial area in East Asia and cause environmental pollution.

In addition to the Kosa events, atmospheric turbid phenomena (like fumes or mists) were occasionally observed in spring in recent years over western part of Japan, characterized by a significant increase in the amount of fine particles (0.3μm~1μm in diameter). These fine particles, which are suspected to cause those turbid phenomena, are not the main components of yellow sand dust, since yellow sand dust particles are composed of 4 μm diameter minerals.

To investigate the origin of these turbid phenomena and the relation between turbid phenomena and Kosa events, we collected atmospheric aerosols every 2-3 hours by using a mini step-sampler from March to June, 2005 in Nagasaki, and analyzed them by PIXE. We also used an optical particle counter to determine the size distribution of aerosols. Time series of elemental concentration and particle number concentration was observed.

Experimental

Sampling

Aerosol particles were collected at the campus of Nagasaki University (32.78°N, 129.87°E; 20 m) from March 16 to June 3, 2005, on Kyushu Island in western Japan, where the aerosols affect daily life. A mini step-sampler, of which details were presented in previous paper[1)], was used for aerosol collection. Aerosol particles were collected on a 1μm pore size Nuclepore filter[2)] with the constant face velocity of 80m/min. The effective 50% cutoff diameter of the sampler was less than 0.2 μm[3)] and was sufficient for collecting fine particles. During those 3 months, and with a sampling resolution of 2 or 3 hours, the mini step-sampler collected more than 900 aerosol samples on Nucrepore filter of 200×200 mm^2. Since the mini step-sampler is single stage, an optical particle counter (OPC) was used together with the mini step-sampler.

Analysis

We performed elemental analysis of each aerosol particles using an in-air PIXE analysis system at Tohoku University[4,5)]. The system consists of a beam exit assembly[2)], two Si(Li) detectors and X-Y sample stages. Proton beams were extracted from a Kapton exit window of 12.5 μm. The samples were placed at 1 cm from the exit window and on the X-Y stage in air.

Two X-ray detectors were set at the left side and right side with respect to the beam axis respectively, and their observation angle was 135 degrees with respect to incident beam direction and their observation position was 16mm away from the sample. The first detector (LS60148, Princeton Gamma-Tech) has a large sensitive area and is suitable for trace elemental analysis. To reduce the deformation of the spectrum by recoil protons and pile-up events, a 300 μm thick Mylar filter was used. This detector is used to detect X-ray of energy higher than 5 KeV. The second detector (LS10138, Princeton Gamma-Tech) has a higher energy resolution (138 eV), a thin Be entrance window and a small sensitive area of 10mm^2, and it is suited for the detection of elements of low atomic number ($Z < 25$). Since the intensity of low energy X-ray is too high in this application, a 500 μm thick Mylar filter with a pin-hole of 0.7 mm in diameter was attached to the front of the detector to reduce X-ray counting rate and recoil protons.

Typical X-ray spectra obtained by the detectors are shown in Fig. 1. The system is capable of detecting X-rays ranging from 1.4 to 30 keV with good energy resolution and

detection efficiency. Since elemental concentrations of aerosol samples strongly depend on samples, beam currents in a conventional detector system have to be controlled in correspondence with X-ray counting rate. The present system allowed us to obtain data without changing the beam currents.

The total number of collected aerosol samples was more than 900. Since aerosols were continuously collected under various kinds of atmospheric conditions, analyses of all these samples would have taken too much time. We consequently used the OPC to select the samples to be analyzed, according to their particles number concentrations (exceeding 50 million/L for fine particles and 100/L for coarse particles). The days of March 22, 31, April 3, 15, 16, 21, 22, May 3, 12, 23 and June 2 were selected, representing a total of 140 samples that we analyzed afterwards. For quicker analyzes, we introduced an automatic measurement system which collects data until a fixed charge, saves data and changes the sample in a definite order.

Energy of the proton beam is 3 MeV and beam spot size is 1.5 mm in diameter with a beam current of ～1.5 nA, for a total accumulated charge of 0.4 μC. Quantitative PIXE analysis was performed using external standard method[6]. A program based on pattern analysis was them usud to analyze PIXE spectra.

Result and Discussion

Aluminum, silicon, sulfur, calcium, iron, zinc, lead, mercury and bromine were detected, where bromine is a component of the Nuclepore filter. Concentrations for fine (0.3 and 0.5 μm) and coarse (1, 2 and 5 μm) particles are shown in Figs. 2 and 3, respectively with daily average elemental concentrations. Concentrations of fine and coarse particles show different trends. Fumes and mists were observed on 2 April, 12 and 23 May, when fine particles reached its highest concentrations. On 15, 16, 21, 22 April and 12 May, Kosa events occurred, meaning that fine particles are not correlated with yellow sand dust particles. Elemental concentrations of Si, Ca, Fe, Pb and Hg show similar trends to that of coarse particles, whereas variations of elemental concentrations of S and Zn and fine particles are almost same. It is consequently apparent that coarse particles contain Si, Ca, Fe, Pb and Hg and fine particles contain S and Zn. Figure 4 shows time variations of elemental concentrations and concentrations of fine and coarse particles on April 21 when both fine and coarse particles showed their highest concentrations. It is apparent that the time variations of fine particles are different from that of coarse particles. It also shows

that Aluminum, silicon, calcium, iron, lead and mercury are related to coarse particles, whereas sulfur and zinc are well correlated with fine particles. On April 22, coarse particles presented higher concentrations but fine particles showed lower concentrations. In this case, no correlation was seen between elemental concentrations of sulfur and zinc with number of concentrations of fine particles. On the other hand, on May 23, coarse particles and fine particles showed lower and higher concentrations, respectively. In this case, there was no correlation between coarse and elemental concentrations. Backward trajectory analysis using NOAA HYSPRIT[7)] indicated that the particles collected on these days came from the Chinese coastal area to Nagasaki. This therefore proves that fine particles are composed of anthropogenic sulfate aerosols and caused fumes and mists in Nagasaki. Zinc is also an anthropogenic aerosol related to industry, whereas silicon, aluminum, calcon and iron are minerals and components of yellow sand dusts and thus were contained in coarse particles. The coarse particles were also transported from Asian continent over the Chinese industrial area to Nagasaki. Therefore lead and mercury were also contained in coarse particles and are inferred to have been adsorbed through mixture with coarse particles during transportation.

Conclusion

We collected aerosol particles with a mini step sampler for more than two months. We selected some samples using OPC observation data and analyzed them using our automatic PIXE measurement system, which is very useful for numerous samples analyses. As a result, Aluminum, silicon, sulfur, calcium, iron, zinc, lead and mercury were detected in aerosol samples. Moreover, concentrations of fine and coarse particles showed different trends: Kosa events occurred when coarse particles reached high concentrations, and elemental concentrations of Si, Ca, Fe, Pb and Hg showed similar variations along with that of coarse particles. Si, Ca and Fe are main components of yellow sand dusts whereas Pb and Hg are inferred to have been adsorbed through mixture with coarse particles during transportation. Concentrations of fine particles were also correlated with concentrations of S and Zn, showing us that sulfate aerosols cause turbid phenomena in western Japan. In addition, we also showed that PIXE analysis of aerosol particles collected with the mini step sampler is very effective for a better understanding of such turbid phenomena.

Reference

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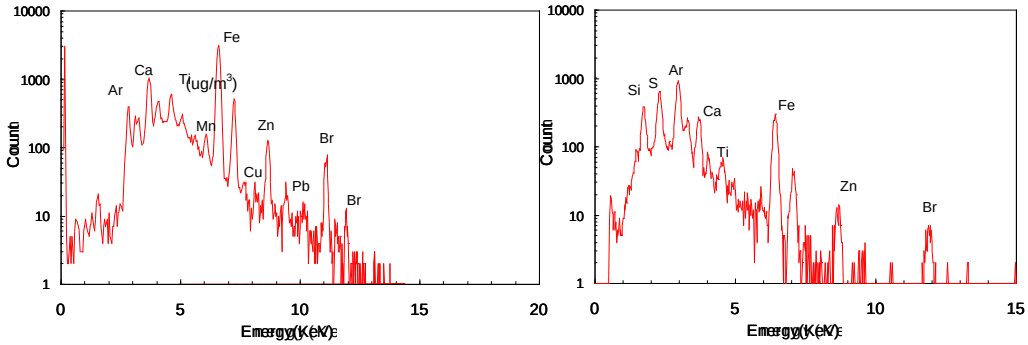


Figure 1. PIXE spectra of aerosol sample collected on 21 April, 2005.

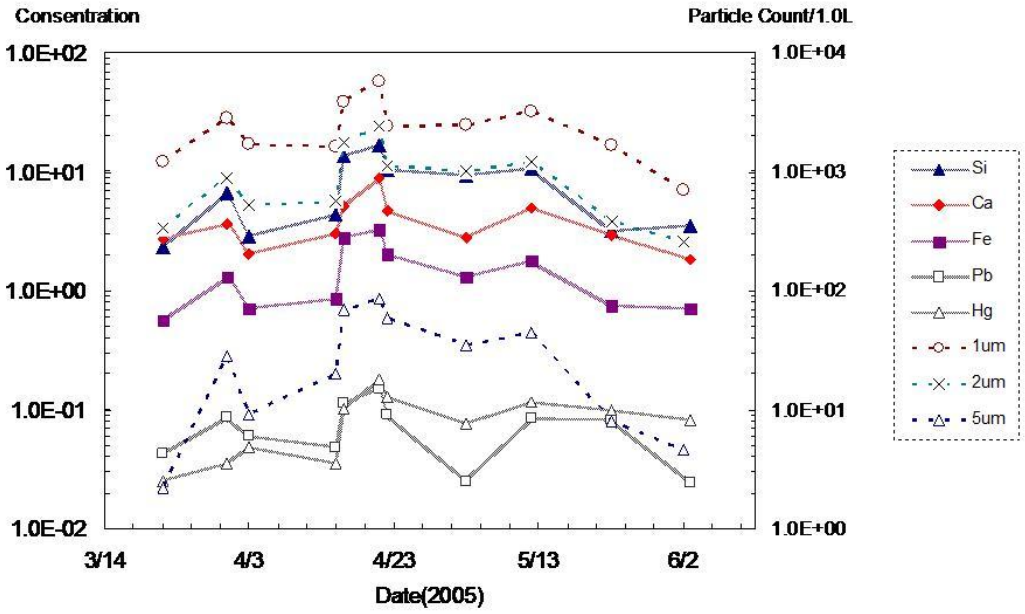


Figure 2. Elemental concentrations related to coarse particles.

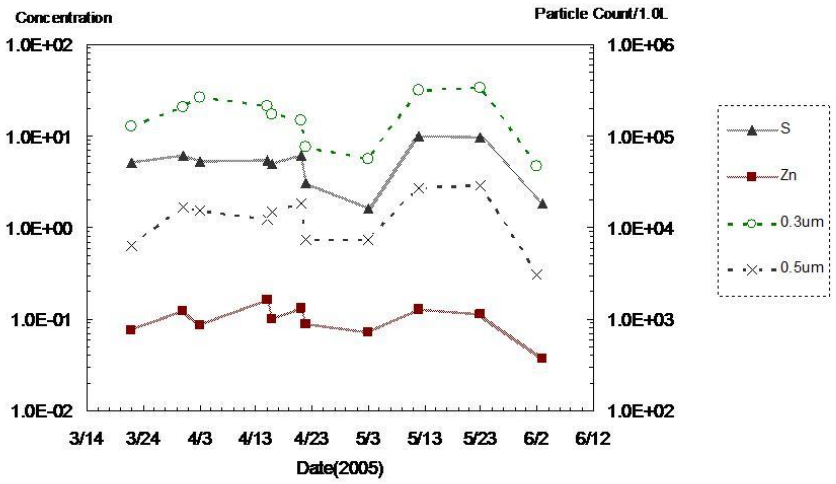
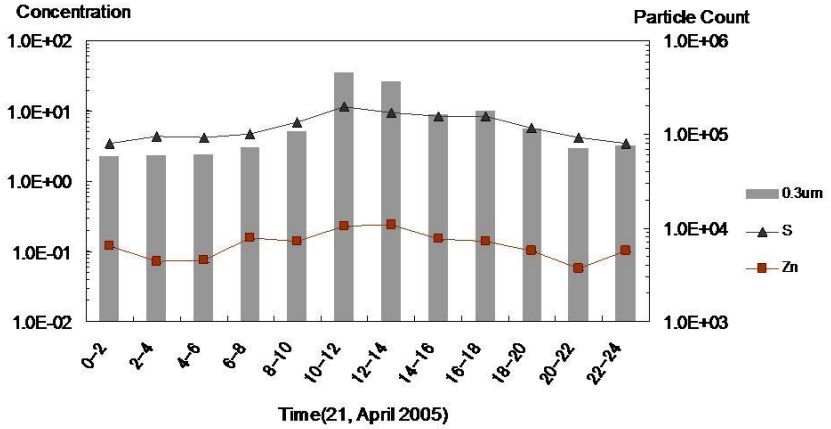


Figure 3. Elemental concentrations related to fine particles.



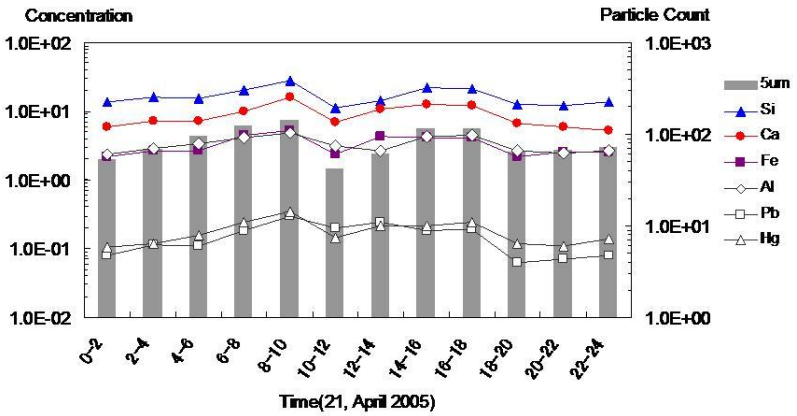


Figure 4. Changes of elemental concentrations and number of concentrations of fine and coarse particles on 21 April.