Record for Long-range Transport of Fly-ash Particles during Past 100 Years in the Pond Sediments in Oki Islands, Japan Sea

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Fly-ash particles such as spheroidal carbonaceous particles (SCPs) and inorganic ash spheres (IASs) in sediments indicate modern fossil fuel combustion. A lake or pond away on the leeward of industrialized areas accumulates these particles in sediments to record the temporal change of fossil fuel combustion in the industrialized areas. The authors analyzed the fly-ash particles in a sediment core from Oike Pond in Oki Islands in the Japan Sea. The age of the core covers the last 100 years. The amount of both SCPs and IASs gradually increases from 1950s to the present. SCPs appear for the first time around the 1950s, while IASs have appeared around the 1920s. The profiles of lead and mercury concentration are similar to the profiles of the fly-ash particles. This evidences the increase of air-pollutants by coal combustion. The primary source of the IASs and SCPs is supposed to be coal combustion. The SCPs profile from Oike Pond resembles to that of Taihu Lake in eastern China after 1950s. Therefore the IASs deposited in Oike Pond after 1950s are inferred to have derived from China following increased coal consumption.

Keywords : long-range transport, coal combustion, spheroidal carbonaceous particles (SCPs), inorganic ash spheres (IASs), Oike Pond

I. Introduction

Over the last twenty years Japanese atmospheric environment researchers have reported the airborne material from China where coal combustion occurs on an enormous scale (*e.g.* Mukai *et al.*, 1990, 1994 ; Murano *et al.*, 2000). The Japanese Islands located in the east of the Asian continent are constantly under the westerly wind from the continent. Recently, thirteen countries in East Asia including Japan organized the EANET (Acid Deposition Monitoring Network in East Asia) which aims to understand the long-range transport of air pollutant and to facilitate cooperation among the member countries. Though EANET launched the monitoring of present-day air pollutant

transportation in Asia, little research has been carried out to reveal temporal change of the pollution on a long time scale.

Lake sediments accumulate various materials in atmospheric precipitation. In particular, the fly-ash particles generated by fossil fuel combustion are well preserved in sediments. Fly-ash particles are produced by the high temperature combustion of fossil fuels. They comprise two particle types of spheroidal carbonaceous particles (SCPs) and inorganic ash spheres (IASs) (Rose, 2001, Fig.1). They are useful indicators of the fossil fuel combustion after the industrial revolution.

SCPs are porous spheroids of mainly elemental carbon (Goldberg, 1985) and are produced by the combustion of coal and oil. IASs are fused

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Fig. 1 SEM images of SCPs (left) and IASs (right) in Oike Pond sediments

inorganic spheres formed from the mineral component of coal fly ash (Raask, 1984). IASs are generally greater in quantity and smaller in size than SCPs. IASs has a diameter of less than $20\mu\text{m}$ (McElroy *et al.*, 1982), while SCPs has a diameter of less than $100\mu\text{m}$ (Raask, 1984). Consequently, as compared to SCPs, IASs have the potential to travel further in an air stream and act as a better indicator of anthropogenic pollution and impact in remote areas. However, the morphology and chemical constituents of the IASs from combustion and those from natural sources such as volcanic emissions and micro-meteorites are similar. Hence, there are a few studies using IASs. (*e.g.* Rose, 1996 ; Alliksaar and Punning, 1998). These studies are about the spatial distribution of fly-ash and trace metals in Estonia and the relation of SCPs and IASs in U.K. respectively.

In recent years many researchers have analysed SCPs in sediments from all the continents (details in Rose, 2001) but in Japan only Murakami and Inoue (2004), Murakami *et al.* (2004, 2005) have worked on SCPs.

In this study, the authors acquired a sediment core representing the last 100 years for analyses from a pond in Oki Islands isolated in the Japan Sea. The islands are not industrialized and are located in the windward of Japan away from any heavily industrialized area. This paper describes the temporal trend of SCPs and IASs in the last about 100 years in Oike Pond in Oki Islands.

II. Coring site and analytical method

1. Site and lithostratigraphy

Oki Islands are located about 50 km north in

the Japan Sea off Shimane in western Honshu. The authors collected a sediment core in Oike Pond at $36^{\circ}12'10''\text{N}$ and $133^{\circ}22'8''\text{E}$ under 6.3 m of water in the southeast side of Dogo Island in July 2003 (Fig. 2). Oike Pond is a freshwater pond isolated from the sea by a beach ridge and its area is 0.039 km^2 . In Oki Islands there is a small internal-combustion power station for about 17,000 people and local industries, but there is no large source of fly-ash particles such as a thermal power plant using pulverized coal particles and oil droplets.

A sediment core was collected using an acrylic tube of 110 cm long and 10 cm bore. The 107 cm core mainly consists of clay. The top 5 cm portion disturbed during the coring was cut into two 2.5 cm slices. The rest of the core was cut into 1 cm thick slices and we analysed 45 samples at intervals of 2 cm.

Yamazaki *et al.* (2004) estimated the age of the sediments. Radiometric dates were obtained for these sediments by analysing ^{210}Pb and ^{137}Cs ratio using an ORTEC HPGe detector (LO-AX/30P) coupled to a 4,096 channel multi-channel analyser. All 104 samples were dated and dates were calculated on all levels. The details of the methods and the chronologies of the core have been reported by Yamazaki *et al.* (2004).

2. SCP and IAS analyses

The analytical procedures of SCPs and IASs of this study are improved from that of Rose (1990, 1994). SCPs are mostly composed of elemental carbon, and although they are physically fragile, they are chemically robust. Hence, organic, siliceous, and carbonate materials were removed by 60% concentrated nitric acid (HNO_3), 46% hydrofluoric acid (HF), and 6 M hydrochloric

Fig. 2 Map showing the sampling location of this study

ric acid (HCl), respectively. IASs are composed mainly of fused almino-silicate minerals composed of SiO_2 , Al_2O_3 , Fe_2O_3 and other oxides. Organic materials, biogenic silica, and carbonate were removed by 10% hydrogen peroxide (H_2O_2), 0.3 M sodium hydroxide (NaOH), and 3 M hydrochloric acid (HCl), respectively. Further, in each procedure, solution of suspended microspheres (Ogdens III, 1986) were added in order to count these particles. The final residue is evaporated on a slide glass, mounted on a microscope slide, and counted at magnification of 200 times under an optical microscope with vertical illumination. The size limit for the identification is $2\mu\text{m}$. The particle concentration is calculated as the number of particles per gram (particles g^{-1}).

III. Results

Figure 3 shows the profiles of SCPs and IASs in Oike Pond sediments. The concentration of SCPs ranges from about 700 g^{-1} to $2,000\text{ g}^{-1}$. The highest SCPs concentration was found in the uppermost part of the core (6–7 cm). The SCPs concentration continuously increases upward from the horizon of 47–48 cm deep that corresponds to the age around 1950s.

The IASs concentration ranges from about $2,000\text{ g}^{-1}$ to $26,000\text{ g}^{-1}$. IASs are present in all levels in the core. The concentration of IASs is greater than that of SCPs by ten times or more. The highest IASs concentration was found at the horizon of 10–11 cm deep that corresponds to the age around 1990s. The IASs concentra-

tion tends to increase toward the top of the core.

The particle size of counted SCPs particles is within 5 to $40\mu\text{m}$ and that of IASs is within 2 to $30\mu\text{m}$. Most of the particles are $10\mu\text{m}$ or smaller.

IV. Discussion

1. Profiles in last 100 years

IASs are produced both by human coal combustion and by natural sources such as volcanic eruption and meteorite fall. In Figure 3, IASs are detected in the lowest part of the core (ca. 1890s), and the concentration gradually increases from the 1920s to the present. Since there was no coal combustion at high temperature (about 850°C) before the 1920s, the IASs before 1920 are probably from the natural sources.

In 1930s to 1940s, power plants that mainly combusted coal fuel began operation in Japan. Korea and China also started industrial activity in the same period though in a smaller scale. At Oike Pond, the influence of coal combustion by industrial activity has started from this period.

The concentration of IASs and SCPs increases from around the 1950s. SCPs derive only from pulverized coal or oil droplet combustion (Rose, 2001). Therefore, the SCPs emission from large-scale factories such as large power plants became significant during this period of 1950s to 1960s.

The IASs/SCPs ratio provides information on the source fuel types as coal combustion

Fig. 3 Concentration of SCPs, IASs, Pb and Hg, and IASs/SCPs ratio profiles for Oike Pond sediments

produces both SCPs and IASs while oil combustion produces only SCPs (Rose, 1996). In Oike Pond sediments, high IASs/SCPs ratio indicates larger contribution of coal combustion than that of oil combustion.

Yamazaki *et al.* (2004) analyzed heavy metal concentration in Oike Pond sediment core. The profiles show upward increase of lead and mercury concentration caused by anthropogenic contamination. The concentration of lead and mercury increases from 1920s–1930s. The concentration of lead has continued to increase until today, while that of mercury had increased until 1960s and became constant. Mukai *et al.* (1999) pointed out that lead and coal fly ash closely related to coal combustion.

2. Comparison with other study sites

Figure 4 shows the profiles from Osaka Bay (Murakami *et al.*, 2005; Yasuhara and Yamazaki, 2005, location in Fig. 2), Taihu Lake in eastern China (Rose *et al.*, 2004; location in Fig. 2) and Pinkworthy Pond in southern U.K. (Rose and Appleby, 2005).

Osaka is the second biggest metropolitan area in Japan with much agglomeration of heavy and light industries. The profiles of SCPs and IASs in Osaka Bay show rapid increase in con-

centration after 1930s and a peak in early 1960s. The IASs/SCPs ratio in Osaka Bay had been high between 1930s and 1980s and decreased since 1980s. This represents the change in the ratio of coal and oil combustion. The metal concentration of chrome, copper, zinc, and lead also shows a peak between late 1950s to and 1960s (Yasuhara and Yamazaki, 2005). These changes are closely related to the high level of coal consumption around Osaka Bay area in 1960s and before the enforced emission control after late 1960s, and before the transition from coal and oil to natural gas in 1970s.

The profiles of the Osaka Bay sediments are similar to the profile of U. K. (Fig. 4). The profile of U.K. shows rapid increase of fuel combustion after the Second World War and following decrease by emission control. There are many differences between the profiles from Oike Pond and Osaka Bay. This demonstrates that the influence from the industrial sources in and around Osaka is not significant in Oike Pond.

The results of SCPs concentration in Taihu Lake sediments in China (Rose *et al.*, 2004) show rapid increase in concentration in the 1950s, and the high level continued from the 1970s to the 1980s to peak in the 1990s. This feature of

*1 Murakami *et al.* (2005); *2 Yasuhara and Yamazaki (2005); *3 Rose and Appleby (2005); *4 Rose *et al.* (2004)

Fig. 4 Comparison of Osaka Bay (SCPs, IASs, IASs/SCPs ratio and heavy metal elements), SCPs in Pinkworthy Pond in U.K. and SCPs in Taihu Lake in China

Fig. 5 The record of coal and oil consumption in Japan, South Korea and China
Data source : BP statistical review of world energy 2006.

the continuous increase in SCPs concentration is different from the changes observed in Osaka and U.K. The chrome, copper, zinc, lead and SCPs profiles in Taihu Lake are very similar to each other suggesting the profiles represent the regional industrial development (Rose *et al.*, 2004). Those profiles from Taihu Lake are similar to the profiles from Oike Pond after the

1950s.

The temporal changes of SCPs and IASs concentration in Oike Pond sediments resemble more to those from Taihu Lake in China than to those from Osaka Bay and U.K.

Figure 5 shows recent coal and oil consumption in Japan, South Korea and China that surround Oki Islands. Among them, the con-

tinuous increase of coal and oil consumption in China is very remarkable. Also the total consumption far exceeds Japan and Korea. Japan has constantly consumed large amount of oil since 1970s. The increase of oil consumption in South Korea is distinctive after 1990 but the amount is still smaller. The constant increase of IASs after the 1950s in Oike Pond looks similar to the pattern Chinese consumption of coal. Considering the similarities, prevailing westerly winds and geographic location of Oki Islands, China is the most likely source of the fly-ash particles in Oike Pond sediments, though more investigation is necessary to firmly identify the source areas.

V. Conclusion

The vertical profiles of SCPs and IASs in Oike Pond sediment showed that their concentration has been increasing to the present. The profiles of SCPs and IASs corresponded to those of lead and mercury elements that indicate anthropogenic contamination. In Oike Pond, it was shown clearly that the influence of long-range transport started around the 1920s. Furthermore, since the concentration of both particles increased in around 1950s, it is considered that the influence of the large-scale combustion from the neighboring countries especially from China became strong. Future work is required to distinguish the source more clearly. At present, EDS analysis on the surface of a particle is being conducted.

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隠岐諸島溜池堆積物を用いたフライアッシュ粒子 長距離輸送の過去 100 年間の記録

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〔要 旨〕

産業革命以降の人間活動の指標として、球状炭化粒子 (SCPs) と球状灰粒子 (IASs) が用いられる。離島における溜池堆積物中のこれらの粒子は、長距離輸送の指標となる。日本海上の離島である隠岐諸島後男池において柱状堆積物を採取し、化石燃料燃焼粒子である SCPs や IASs を用いて長距離輸送の影響を歴史的に解析した。SCPs・IASs の歴史トレンドは、両粒子とも 1950 年以降現在に向かって増加傾向を示した。SCPs は 1950 年頃、IASs は 1920 年頃から産出しはじめた。これらの粒子の

鉛直変化は、人為汚染を示す鉛や水銀の変化ともよく一致する。これは石炭燃焼による大気汚染の増加を示唆し、男池堆積物の SCPs・IASs は石炭燃焼由来と考えられる。大阪湾やイギリス、中国太湖での研究結果との比較から、男池の SCPs・IASs の鉛直変化と太湖の 1950 年以降の増加傾向が類似することを示唆した。1950 年以降に男池に堆積した IASs は、石炭燃焼が増加している中国からの可能性が考えられる。

キーワード : 長距離輸送, 石炭燃焼, 球状炭化粒子 (SCPs), 球状灰粒子 (IASs), 男池

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