C-1.1.1 Contribution of Transboundary Air Pollution from Asian Continent with Isotope Ratio Determination and Compilation of Deposition Map of Acidic Compounds (Final Report)

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Abstract In order to clarify the behavior of atmospheric pollutants, observations of atmospheric pollutants have been carried out at several places where the air pollutants from Asian continent may reach. In Okinawa Is., annual mean concentration of ozone exhibited a trend of increase from '92 to '95. The δ^{34}Snss of collected aerosol in summertime is about 2 times bigger than that of wintertime indicating that the contribution of emission source that emit heavier S compound dominate in wintertime and the inverse in summer. Long range transport of air pollutants were significantly indicated. As for dry deposition fluxes gaseous compound such as SO_2, HNO_3(g) and NH_3(g) showed a larger dry deposition amount than corresponding particulate matter.

Key Words East Asia, Long Range Transport, Lead Isotope Ratio, Sulfur Isotope Ratio

1. Introduction

A large amount of SO_2 and NO_x which were the precursor of acid rain is emitted in East Asia followed by European continent and Northern America continent. It was forecasted that the emission of SO_2 and NO_x may increase in the near future by the development of industry and increment of population. Therefore, the deposition of acidic component will increase in East Asia. It is anxious that the damage by acid rain expand in East Asia including Japan. From the air pollutant monitoring at less polluted mountainous area and remote islands or the sampling site where the air pollutants from the Asian continent may be transported, we can learn the behavior of air pollutants and can detect the yearly variation of acidic deposition in Japan.

2. Research Objectives

To clarify the transboundary air pollution from the Asian continent to Japan, we conducted ground-based observations. From the air pollutant monitoring at less polluted remote islands(Oki Is., Okinawa Is.) we can learn the behavior of air pollutants and can detect the transboundary air pollution from Asian continent to Japan. We conducted stable isotope ratio determination of lead and sulfur and compilation of acidic deposition.

3. Research Method, Results and Discussion

[1] Okinawa Island (Hedo)

Ozone concentrations were monitored by Dasibi ozone monitor and hourly mean ranged

from 1 to 93 ppbv and average of entire period is 33.9 ppbv. The time variations of monthly mean concentration(MMC) of ozone from October 1991 to December 1995 are shown in Fig. 1. The predominant features are as follows: In January to May, air mass is affected with continental high pressure and marine high pressure, the MMC ranged from 38.9 to 44.1 ppbv. On the contrary, MMC is the lowest of 13.0 and 14.8 ppbv, in July and August, respectively, by the effect of high pressure of Pacific Ocean. From September, MMC increased to 30.7 ppbv by the meteorological condition(low pressure by typhoon and continental high pressure). In October to December, the continental high pressure prevails over Okinawa Is. and the MMC stayed around 39 ppbv.

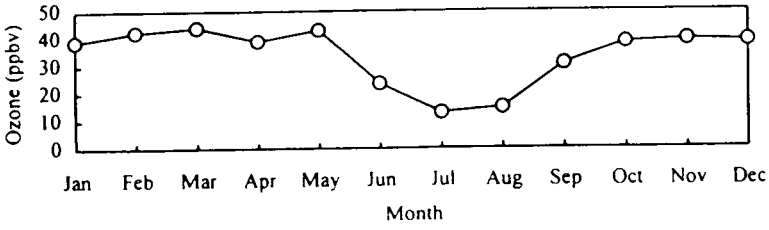

Fig. 1 Monthly mean ozone concentrations from Oct. 1991 to Dec. 1995

The trend of annual mean concentration of ozone(AMC) is illustrated in Fig. 2. Small increase of AMC of 0.3 ppbv is observed from '92 to '93. However, from '93 to '94, more bigger increase of 3.6 ppbv is observed. Once again small increase of 0.4 ppbv is observed from '94 to '95. In general, AMC increase trend is apparent

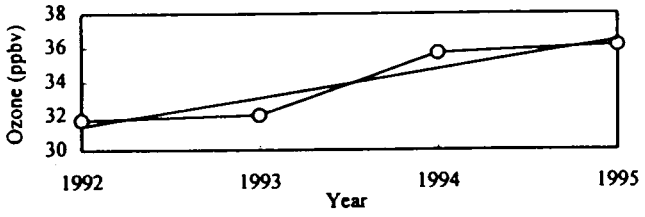

Fig. 2 Trend of annual mean concentration of ozone

[2] Lead Isotope Ratio

Measurement of lead isotope ratios in the air samples in various Asian urban sites, and comparison of the variation of lead isotope ratios observed over Oki islands to the values of source regions were conducted. Lead isotope ratios in the solution were measured by ICP-MS (VG-Elemental).

Lead isotope ratios in several Asian urban sites are summarized in Fig. 3. It was found that most cities showed narrow range but difference in isotope ratios from each other. Although airborne particulate samples were collected from several cities in Japan, the lead isotope ratios in all sites were very close. From this results, it was concluded that lead isotope ratios could be good tracers to show the regional characteristic of air pollution. Figure 4 showed $^{207}Pb/^{206}Pb$ ratio and air trajectories at that time when the sample was collected. Low values of $^{207}Pb/^{206}Pb$ ratio were found when trajectories came from Japan,

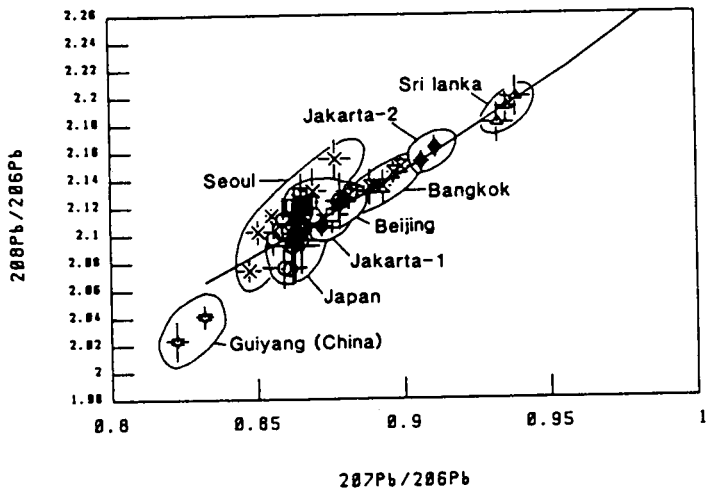

Fig. 3 Lead isotope ratios in Asian urban air

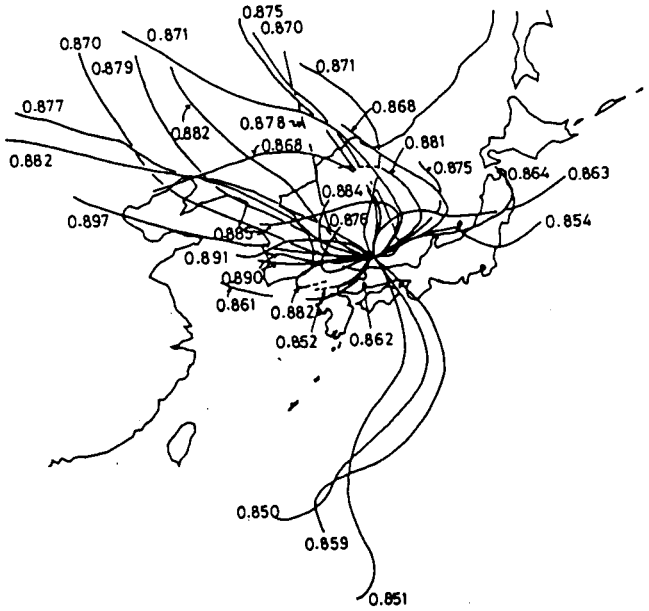

Fig. 4 $^{207}Pb/^{206}Pb$ and corresponding trajectories to sampled air over the Oki Islands[1)]

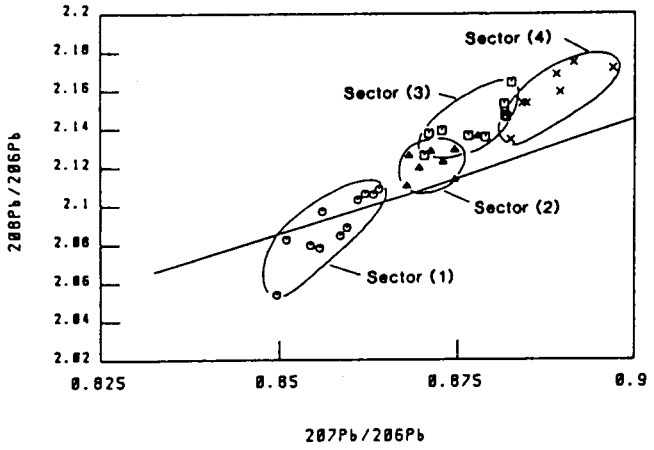

Fig. 5 Classified lead isotope ratio data based on the trajectories shown in Fig. 4.
(sector 1 : Japan, sector 2; Russia, sector 3; China, sector 4; Korean peninsula.)

Table 1 The $\delta\ ^{34}S$ values of SO_2 emitted from volcano

	year	$\delta\ ^{34}S$(‰)		$\delta\ ^{34}S$(‰)
Mt. Sakurajima	1992	+5.2	Satsumaioujima Is.	+10.1
	1992	+8.4	1995(all)	+13.5
	1992	+7.4		+10.6
	1992	+5.6		+12.6
	1992	+4.7		
	1993	+3.2		
	1995	+4.4		

while high values were observed when the trajectories came from Asian continent. These trajectories were classified to 4 sectors and the classified data was plotted in Fig. 5. If we compared this data with the data in Fig. 3, it was found that Japanese sector had very similar values to the data from Japanese cities in Fig. 3. Therefore, different isotope ratios from Japanese cities which were observed in the case in which air came from the Asian continent, showed that different air pollutants from Japanese cities came to the islands at that time.

[3] Sulfur Isotope Ratio

In order to identify the origin of sulfate in the precipitation and high concentration of SO_2, the determination of S isotope ratios of emitted volcanic gases from Mt. Sakurajima and Mt. Satsumaioujima Is.(Table 1). In 1992, the weighted average of $\delta\ ^{34}S$ value is +5.8‰ and higher than those obtained in other 1993 and 1995(+3.2‰ and +4.4 ‰). The activity of volcano is different in 1992 and other years. It is reported that the activity of volcano affects on the $\delta\ ^{34}S$ values of emitted SO_2.

The $\delta\ ^{34}S$ values measured in the volcanic gas from Satsumaioujima Is. ranged from +10.6 to 13.5 ‰ , indicating that it emit ^{34}S abundant volcanic gas. These results indicate that the $\delta\ ^{34}S$ value of Mt. Sakurajima and Mt. Satsumaioujima Is. are not so different from the $\delta\ ^{34}S$ value

Table 2 The difference of δ^{34}Snss values of rain and snow

	δ^{34}Snss(‰)
Rain	1.0
Snow	5.4
Snow/Rain	5.4

those of volcanic gasses(about +5‰). and petroleum samples imported from China and Russia, to evaluate the transboundary air pollution from the Asian continent to Niigata prefecture. We also conducted a field survey to collect atmospheric deposition and aerosol in the mountainous region(Mt. Myokou) which is located in the southwestern part of Niigata prefecture. The δ^{34}S values of coal(China) and coal(Russia) were +8.8±9.2‰ and +4.5±4.9‰, respectively, and they are higher than compared to that(-2.7±4.1‰) obtained in Niigata prefecture from the emitted gasses produced from oil burning factory. The δ^{34}Snss value obtained from rain and snow samples differed a factor of 5 indicating the different origin of rain and snow(Table 2).

emitted from Chinese coal combustion, so it is necessary to use meteorological analysis to assess the effect of continental airpollutant transport to our country. The precipitation collected in Arimura was affected by volcanic ash. The sulfate in the precipitation is considered to be originated from volcanic ash. The δ^{34}Snss value of precipitation sample showed +8.5‰ and is higher compared to Sulfur stable isotope ratio was determined on coal

After the determination of stable isotope ratios of aerosol sulfate collected in Oki Is. in summer and in winter, we evaluated the seasonal variation. The back trajectory analysis of arrived the sampling points at 21:00 LT are used to assess the δ^{34}Snss values(Fig. 6). The

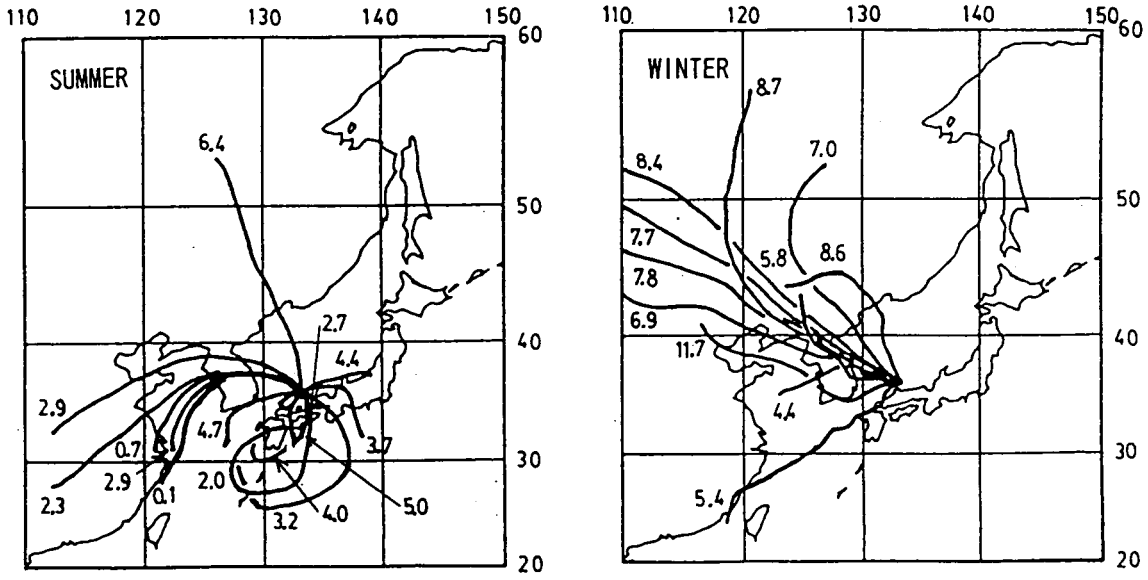

Fig. 6 Back trajectories and δ^{34}Snss of collected aerosol[1)]

^{34}Snss values differed significantly according to the air mass traveled, +7.5±0.96‰ was obtained via northeastern China and North Korea(Sector 1), +3.7±3.4‰ was observed across southeastern China and Korea(Sector 2) and +3.8±1.1‰ was obtained via over Yellow Sea and Japanese Islands(Sector 3). The higher value of δ^{34}Snss is observed and the variation is small when the air is transported from Sector 1. The lowest value of δ^{34}Snss is obtained and the variation is the biggest when the air is transported from Sector 2. Extraordinary big value is perceived when the air flow from Beijing or Tientsin. The higher δ^{34}Snss was obtained across northeastern China and North Korea compared to other samples, indicating the contribution of heavier S compound is bigger for the former than

others.

The δ^{34}Snss values are shown on season and sector in Fig. 7. As for seasonal depen-

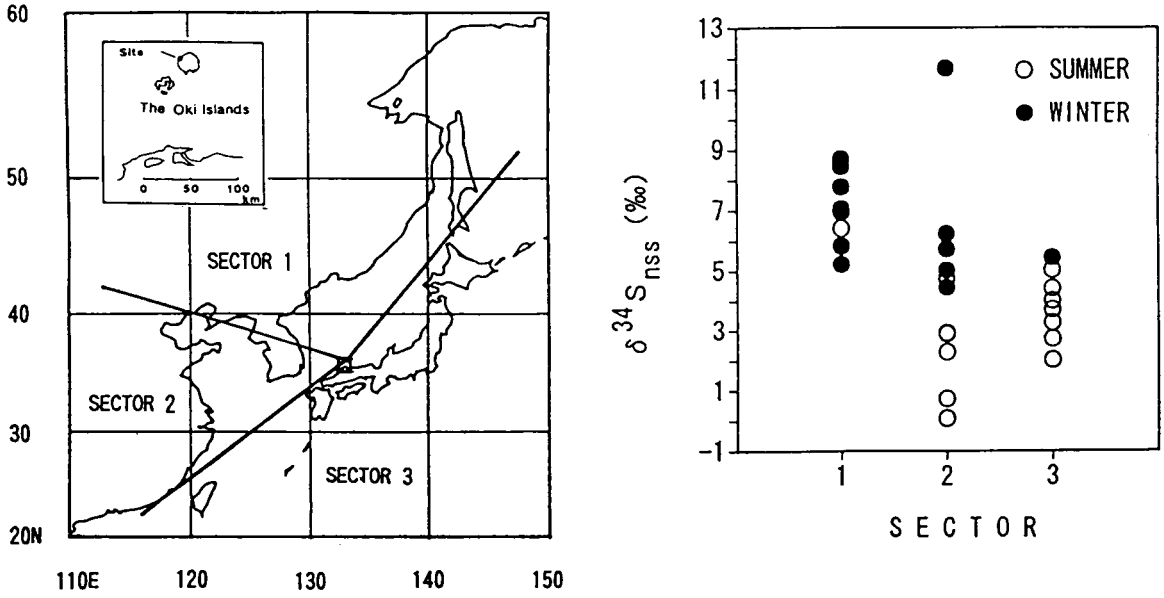

Fig. 7 Seasonal and sector dependence of δ^{34}Snss

dence, δ^{34}Snss of summertime is +3.2±1.7‰ and that of wintertime is +7.5± 2.0‰ and the latter is about 2 times bigger than that of former. This indicate that the contribution of emission source that emit heavier S compound dominate in wintertime and the inverse in summer. Also isotope fractionation effect is the reason of before mentioned results.

[4] Dry Deposition Flux

Much data are compiled as for wet deposition and its spatial distribution is clarified in Japan. However, there are few data on dry deposition. We conducted a field survey to estimate dry deposition amount with inferential method. A filter pack method(1st stage: SO_4^{2-}(p), NO_3^-(p), NH_4^+(p), 2nd stage: SO_2, HNO_3(g), 3rd stage: NH_3(g)) is applied for the determination of ambient concentrations of related air pollutants by one week interval collection during two years.

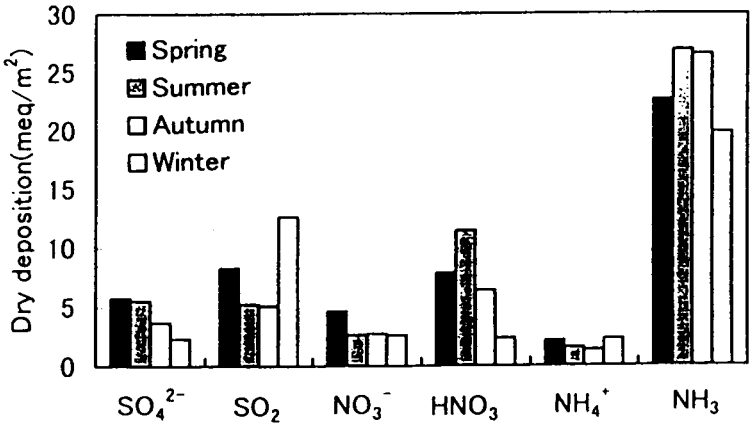

Fig. 8 Seasonal variations of dry deposition fluxes of each chemical component

Dry deposition fluxes are estimated by the inferential method, which require atmospheric concentration and deposition velocities of target chemical species. We adapted dry deposition velocities by the literature. Dry deposition amount of individual chemical species are shown in Fig. 8, on seasonal basis. Annual deposition amount is as follows: SO_2: 31.2, SO_4^{2-}(p): 17.3, HNO_3(g): 27.9, NO_3^-(p), 12.6, NH_3(g): 95.8, NH_4^+(p): 7.33 neq/m^2. Gaseous compound such as SO_2, HNO_3(g) and NH_3(g) showed a larger dry deposition amount than corresponding

particulate matter. It is general feature that the deposition amount of SO_2 is bigger in winter or spring, on the contrary, the deposition amount of HNO_3(g) is bigger in summer.

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