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Elemental compositions and sizes of carbonaceous fly ash particles from atmospheric deposition collected at Cape Hedo, Okinawa, Japan: Implications for their long-range transportation and source region variation

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Abstract

Spheroidal carbonaceous particles (SCPs) are a type of carbonaceous fly ash resulting from high-temperature industrial fossil fuel combustion. In this study, we examined the fluxes, elemental compositions (18 elements including silicon, sulfur, and aluminum but not carbon) and sizes of dry-deposited SCPs in the atmosphere at Cape Hedo (the northernmost part of Okinawa Island) to assess the temporal variation. The study site at Cape Hedo is suitable for investigating atmospherically deposited SCPs, particularly for evaluating their long-range transportation, because Cape Hedo is situated in an outflow region of East Asian pollutants. High SCP fluxes mostly occurred in autumn and winter when air masses came from the Asian continent. Additionally, we determined the temporal variations in the elemental compositions and the sizes of the SCPs during four week-long sampling periods and these results suggest that the high SCP fluxes were due to the transportation of the particles from the Asian continent to the study site. The potential source regions of the particles during respective periods are very consistent with the backward air mass trajectories. Results of our study would imply that sources of the SCPs deposited in the area changed temporarily, and that coarse particulate-pollutants such as SCPs were transported from the eastern Asian continent to Okinawa Island during the periods under specific meteorological conditions. Our findings suggest that the examination of SCPs from atmospheric deposition can contribute to the assessment of atmospheric transportation, specifically for particulate pollutants in the atmospheric boundary layer.

Keywords: Spheroidal carbonaceous particles, Carbonaceous fly ash particles, Atmospheric deposition, Particulate pollutants, Cape Hedo, Transboundary pollution

1. Introduction

Long-range atmospheric pollutant transportation has been a concern during recent decades, particularly in East Asia. In the case of long-range transportation of fine particulate matter including PM 2.5, it is mostly transported along with the movement of stable air masses in the free troposphere. Thus, their transportation process has been assessed using modeling systems, light detection and ranging, and atmospheric pollutant observation in remote areas (e.g., Matsuki et al., 2003; Sakai et al., 2003; Osada et al., 2014; Lun et al., 2014; Wang et al., 2017a, b). Meanwhile, coarse particulate matter of a size range of approximately ten to several tens of microns generally transports in the atmospheric boundary layer (ABL) where the air mass is unstable owing to convection and turbulence (e.g., Choi and Choi, 2008; Li et al., 2013; Wang et al., 2017a, b; Zhang et al., 2018). During regional-scale, long-range transport events, significant fractions of pollutants are frequently transported through the ABL among countries in Northeast Asia (Song et al., 2007; Park et al., 2014). Assessing the long-range pollutant transportation process through the ABL is important to accurately evaluate the pollutant distribution in this region. However, the transportation process in the ABL of these pollutants remains unclear.

Spheroidal carbonaceous particles (SCPs) are a type of carbonaceous fly ash particle, with a size ranging from several to tens of microns originating from industrial high-temperature fossil fuel combustion (Rose, 2001). SCPs can be identified on the basis of their characteristic morphology (Rose, 2008). Although the SCP transportation range is highly dependent on their size (Larsen, 2003; Vukic et al., 2006; Inoue et al., 2013), some SCPs can travel thousands of kilometers in air streams and their presence has been recorded in lake sediments in remote locations such as Greenland, the Falkland Islands, and Antarctica (Bindler et al., 2001; Rose et al., 2012). SCP elemental compositions generally differ depending on their original fossil fuel type (oil, coal, or oil shale). Thus, several studies have examined the elemental compositions of these particles to determine their original fuel type (Rose, 1994; Rose et al., 1994, 1996, 1999b; Alliksaar et al., 1998; Murakami-Kitase et al., 2010; Momose et al., 2012; Inoue et al., 2014).

Inoue et al. (2014) examined the elemental compositions of SCPs collected from modern sediments in the main Northeast Asian cities. The result shows that the elemental compositions of the particles collected from China are significantly different from those from Japan, South Korea, and Taiwan because of the consumption difference in the primary fuel types among the countries or the regions. Additionally, researchers compared the elemental compositions of SCPs collected from Northeast Asian cities to those collected from the remote islands of the Sea of Japan and East China Sea. They reported similarity between the elemental compositions of most particles

collected from China and some of the particles from the remote islands. This similarity implies that the SCPs deposited on the remote islands have been possibly transported from Chinese industrial areas. However, these SCPs are considered to be generally transported through the ABL given their size. This suggests that examining the elemental compositions and sizes of SCPs from atmospheric deposition can contribute to a better understanding of particulate behavior in the ABL, specifically their long-range transportation. Although SCPs in sediments (e.g., from lakes, ponds, and bays) have been extensively and globally studied (e.g., Rose and Juggins, 1994; Rose et al., 1994, 1998, 1999a, 2003, 2004, 2012; Wik and Renberg, 1996; Alliksaar and Punning, 1998; Yoshikawa et al., 2000; Chirinos et al., 2006; Murakami and Yoshikawa, 2007; Landers et al., 2008; Nagafuchi et al., 2009; Murakami-Kitase et al., 2010; Hirakawa et al., 2011; Momose et al., 2012; Murai et al., 2013; Inoue et al., 2014; Engels et al., 2018), SCPs from atmospheric deposition have scarcely been examined (Kaasik et al., 2005).

In this study, we examined the elemental compositions and sizes of SCPs deposited at Cape Hedo on the northernmost part of Okinawa Island, Japan, to assess the temporal variation of their source regions focusing on their long-range transportation from the eastern Asian continent. Cape Hedo is situated in an outflow region of East Asian pollutants (e.g., Kunwar et al., 2016). No major anthropogenic activity was close to the sampling location (Yamamoto and Kawamura, 2011). Thus, many atmospheric environmental studies have been conducted at Cape Hedo to assess long-range transportation (i.e., transportation from the Asian continent) of pollutants and other matters (e.g., Suthawaree et al., 2008; Sato et al., 2008; Handa et al., 2010; Yamamoto and Kawamura, 2011; Ueda et al., 2011; Lun et al., 2014; Osada et al., 2014; Yuba et al., 2014; Shimada et al., 2015, 2016; Kunwar et al., 2016; Zhu et al., 2016; Itahashi et al., 2017). Cape Hedo is a suitable site for investigating atmospherically deposited SCPs particularly for evaluation of their long-range transportation.

2. Materials and methods

2.1 Sampling location and materials

Okinawa Island is along the boundary between the East China Sea and Pacific Ocean (Figure 1). The island has no large industrial area. Potential SCP sources of coal-/oil-fired power plants and oil refineries are situated in the southern part of the island (Figure 1). Some of the SCP potential-sources of the fired power-plants are ~50 km from Cape Hedo where atmospheric deposition samples were collected.

For SCP analysis, we used atmospheric deposition samples collected by Osada et al. (2014). Dry and wet atmospheric deposition samples were obtained weekly from October 2008 to January 2011 at Cape Hedo

(26.86°N, 123.25°E; Figure 1) using a sampler that can automatically separate wet and dry deposition, each of which is equipped with a precipitation sensor (US-330; Ogasawara Keiki Seisakusho Co., Ltd.).

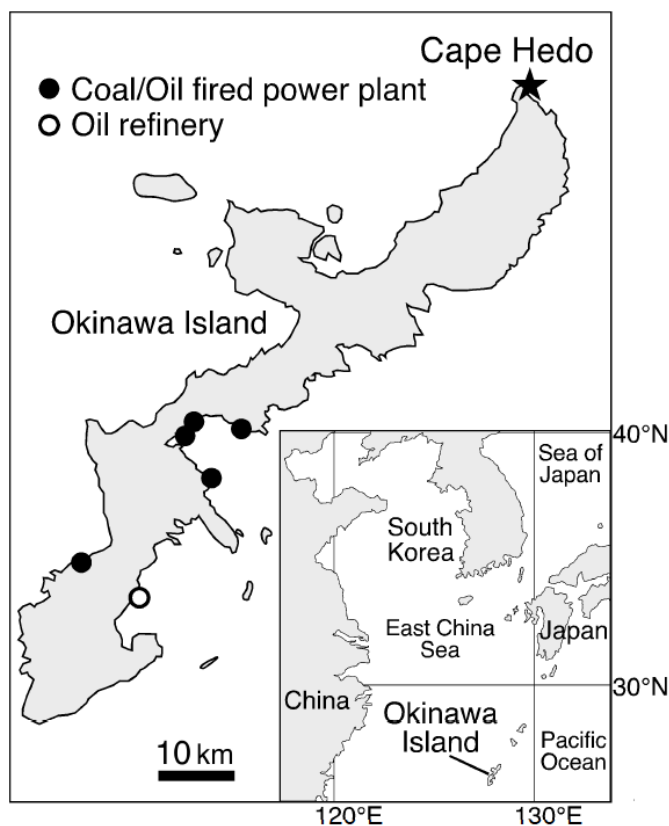


Figure 1 Map of Okinawa Island showing the sampling site (Cape Hedo) and potential SCP sources (coal-/oil-fired power plants and oil refinery) on the island. The location of the island is shown in the map of Far East Asia at the lower right corner.

2.2 SCP analysis

A total of 197 samples (i.e., 97 dry and 100 wet deposition samples) were briefly observed using a light microscope. Based on this observation, 14 dry and 6 wet samples with abundant deposited particles were selected for counting SCPs. For counting SCPs, ~10% of the areas of the respective filter samples were carefully observed using a microscope to approximately evaluate SCP fluxes during these periods. We observed particles on the filter at $\times 200$ and $\times 500$ magnification under incident light using an optical microscope. Referring to Rose (2008), we identified SCPs as black, rounded particles with many pores and a characteristic glossy appearance. We identified nine periods with SCP fluxes of ≥ 400 grains/day·m² and they were designated as high SCP flux periods (Supplementary Data S1): Dry samples collected during the periods November 21–26, 2008; November 26–December 3, 2008; December 24–31, 2008; May 27–June 3, 2009; September 2–9, 2009; December 2–9, 2009; January 6–13, 2010; September 29–October 6, 2010; December 8–15, 2010. In the other periods, the SCP fluxes

were relatively low. The estimation was ≤ 200 grains/day·m². Considering the errors (standard deviations) of the estimated SCP fluxes (see Supplementary Data S1), significant difference between the nine high flux periods and the others was observed. Three out of the nine sample periods with high SCP fluxes were selected for SCP elemental analysis in this study (November 26–December 2, 2008; September 29–October 5, 2010; December 8–14, 2010). In addition, a dry sample with low SCP flux (September 22–30, 2009) was subjected to elemental analysis to compare the SCP elemental compositions in the high and low flux periods. Consequently, for the elemental analysis we used four dry samples collected during the periods November 26–December 2, 2008 (Period 1); September 22–29, 2009 (Period 2); September 29–October 5, 2010 (Period 3); and December 8–14, 2010 (Period 4).

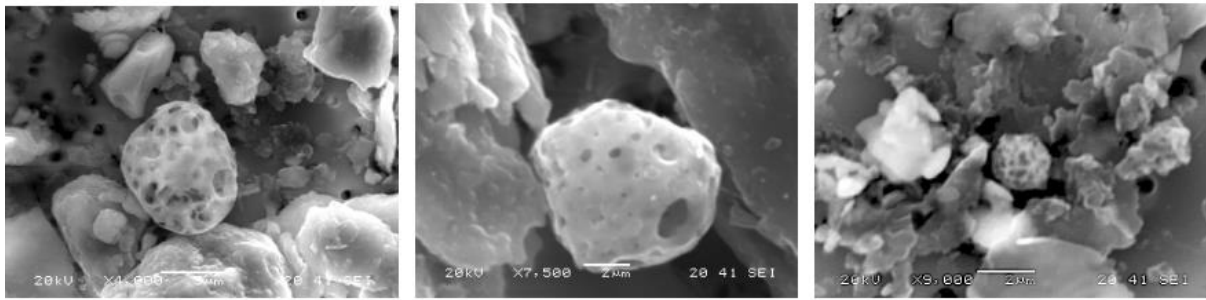
A part of each filter sample was cut and used for SCP elemental analysis. Part of each filter was coated with a thin carbon layer. Thereafter, both observational and elemental SCP analysis were performed using the JEOL JSM-5500 scanning electron microscope (SEM) equipped with an EDAX–energy dispersive spectroscopy (EDS) system (CDU-LEAP detector; Genesis Software) at the Department of Geosciences, Osaka City University, Osaka, Japan. The SEM was operated at an acceleration voltage of 20 kV and a beam current of 500 pA. We used the EDS to quantitatively analyze the Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn concentrations. During this process, the characteristic X-ray intensities were set using the ZAF correction method. The ZAF correction method is a method used to quantitatively estimate the percentages of the respective elements while correcting for the effects of atomic number, absorption, and fluorescence excitation. All the particles (including SCPs and other fractions) were observed on an area of the filters using a SEM to detect at least 10 SCPs in each sample. The SCP identification was restricted to rounded particles with many pores (Figure 2) and these particles were analyzed. The fractions on the filters at over $\times 1000$ magnification were observed, so that small SCPs would not be missed. Elemental compositions (weight%) were obtained at four points for a particle and one outlier was removed. The average percentage of each element at the remaining three points was then calculated. This was because the elemental composition for some particles at one point was some different from those at the other three points.

2.3 Backward trajectory analysis

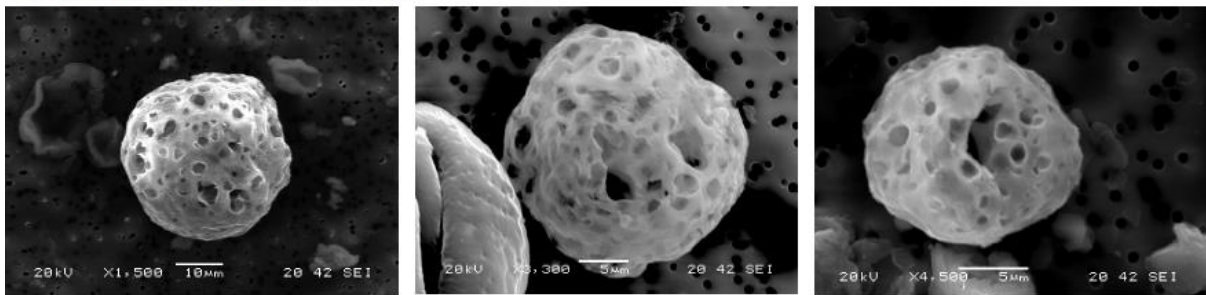
To assess the SCP sources during the respective nine periods with high SCP fluxes and the period with low SCP flux (September 22–29, 2009), we reviewed the backward trajectories of air masses for 72 h during the periods at

the sampling site (Cape Hedo: 26.86 °N, 123.25 °E), starting at 500 m altitude for 72 h every 12 h (00:00 UT),

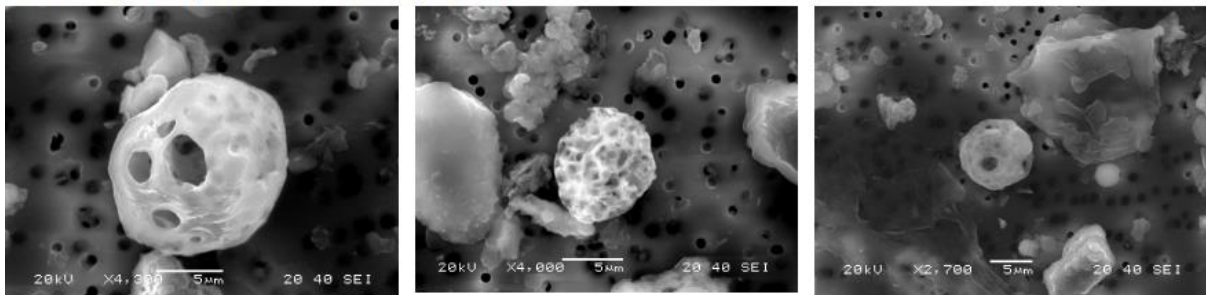
Period 1 (26 November–2 December 2008)



Period 2 (22–29 September 2009)



Period 3 (29 September–5 October 2010)



Period 4 (8–14 December 2010)

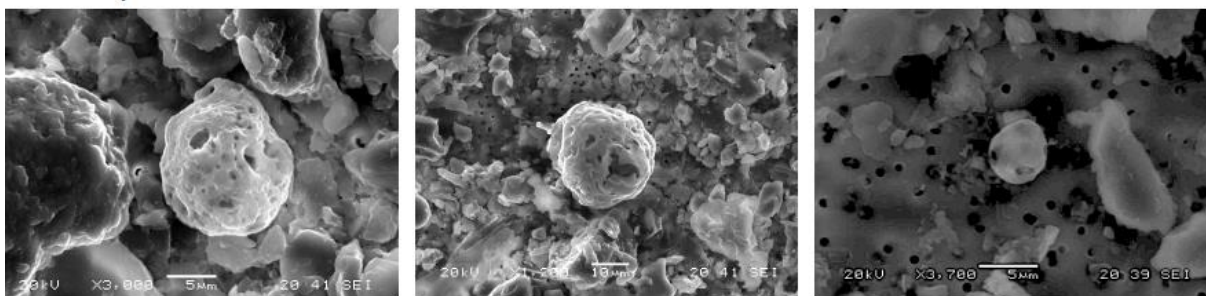


Figure 2 SEM photographs of SCPs found in respective samples during Periods 1–4.

through HYSPLIT vertical velocity model (Stein et al., 2015), using GDAS meteorological data. We also checked backward trajectories of air masses every two weeks in respective months from October 2008 to January 2011 of the sampling duration (supplementary information S2).

3. Results and discussion

3.1 SCP elemental compositions and sizes during respective periods

We obtained the elemental compositions of 12–13 SCPs in respective samples of Periods 1–4 (Figure 3; supplementary information S1). The boxplots of the proportions of the major elements and sizes for the SCPs from the respective periods are also shown in Figure 4 to indicate the overall range of values for particles during each period. We applied a Mann–Whitney pairwise test to the percentages of sulfur in the SCPs during the four periods using Past software (Hammer et al, 2001; available at <https://folk.uio.no/ohammer/past/>) because the percentages are distinctly different among the particles. The test showed that there were significant differences among the four periods ($p < 0.01$) except for Period 3 vs, Period 4 ($p > 0.05$), indicating that the particle elemental characteristics differ among the four periods with the exception of the similarity between those in Period 3 and 4 (supplementary information S3). We applied cluster analysis to particle elemental compositions to group particles with similar elemental characteristics (Figure 5). Based on these results, the particles were divided into four types, namely A, B, C, and D (Figures 3 and 5). Type A particles are characterized by an abundance of S (60–95%). Type B particles are primarily associated with some percentages of both S (30–60%) and Si (20–40%) in combination with 10–20% of Al; the percentages of S are higher than Si in the respective particles.

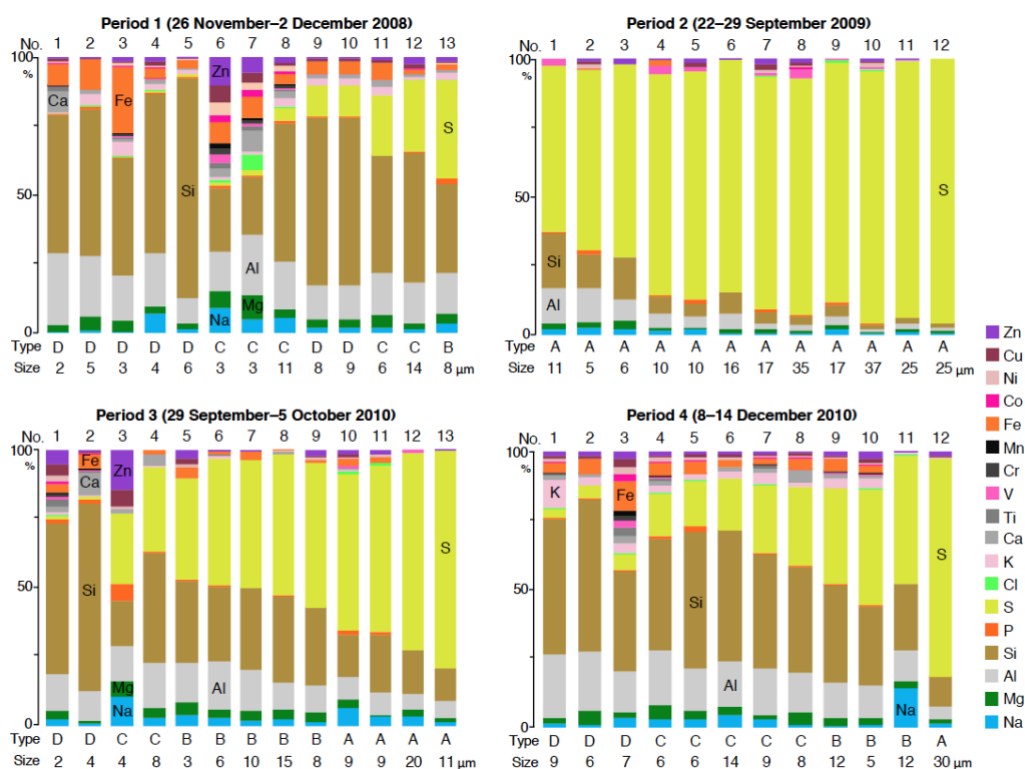


Figure 3 Proportions of the elemental compositions and sizes of respective SCPs in samples collected during Periods 1–4 obtained using an SEM equipped with an EDS system. Types A, B, C, and D are based on the results of the cluster analysis applied to the proportions of the elements in the SCPs (Figure 5).

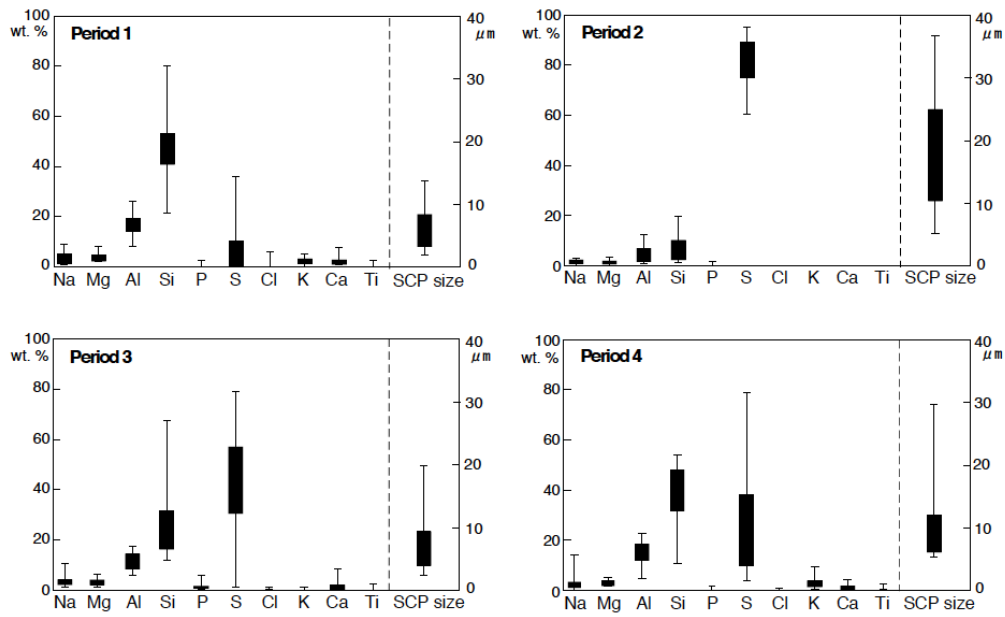


Figure 4 Boxplots indicating the proportions of the main elements and sizes of the SCPs in the samples collected during Periods 1–4. The lower and upper limits of each bar indicate the maximum and minimum percentages, respectively, for each element and size. The box range is between the 25th and 75th percentiles.

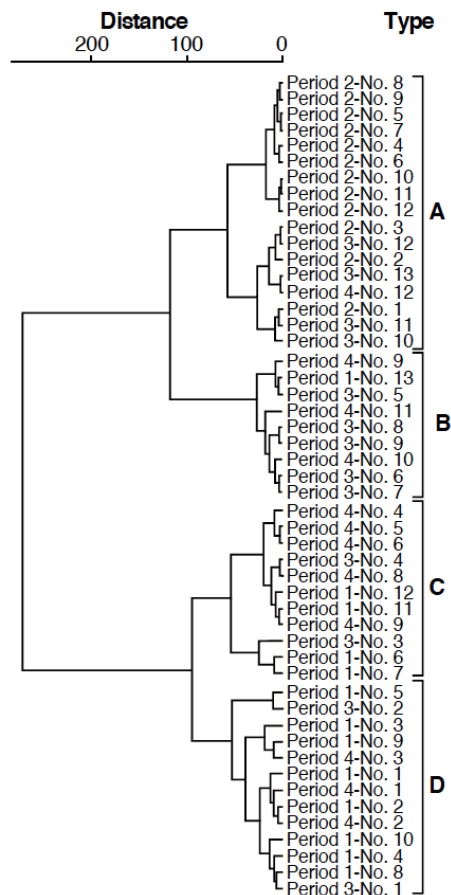


Figure 5 Results of the cluster analysis of the proportions of the elements of respective SCPs. All of the SCPs were divided into four types, namely, A, B, C, and D, based on the clustering results. For the cluster analysis, Ward's method was applied as the algorithm using Past software (Hammer et al, 2001; available at <https://folk.uio.no/ohammer/past/>).

Type C particles are also characterized by certain percentages of S and Si with 10–20% of Al similar to the Type B particles. However, the percentages of Si are higher than S in the respective particles. Lastly, type D particles are characterized by an abundance of Si (40–80%) with 10–20% of other elements, such as Al, S, and Fe.

SCPs of Period 1 are mostly characterized by a dominance of Si with certain percentages of Al and small sizes of less than 10 μm , which are mostly classified as type C or D. Meanwhile, all of the SCPs of Period 2 are characterized by extremely high percentages of S with some percentages of Si and Al, all of which are classified as type A. The sizes of most of the particles exceed 10 μm , and some greater than 20 μm . The SCP elemental compositions and sizes for both Period 3 and 4 significantly vary depending on the particle. Thus, the samples of these periods include all particle types.

3.2 Backward trajectories of air masses reaching the sampling site during respective periods

The results of the backward trajectory analysis during the nine periods with high SCP fluxes are shown in the Supplementary Data S4. Most of the high SCP flux periods occurred in autumn and winter (October to January). In these periods, the trajectories were characterized by the dominance of air masses coming from the northwest. In contrast, as shown in Supplementary Data S2, summer (June to August) had low SCP fluxes with air masses mostly coming from the south or the east. These findings imply that air masses coming from the northwest tend to lead to high SCP fluxes although the air masses from the northwest may have not necessarily resulted in the high SCP flux at the sample site.

The backward trajectories of the air masses in the four periods that were examined for the elemental compositions of the SCPs are shown in Figure 6. During Period 1, the trajectories showed air masses mainly passing through Eastern China. Meanwhile, during Period 2, all of the air masses passed over the Pacific Ocean. During Periods 3 and 4, the trajectories of the air masses varied; nearly one-half of the trajectories passed over Northeast or East China, similar to the trajectories during Period 1, while the other half passed over Okinawa Island and the Pacific Ocean.

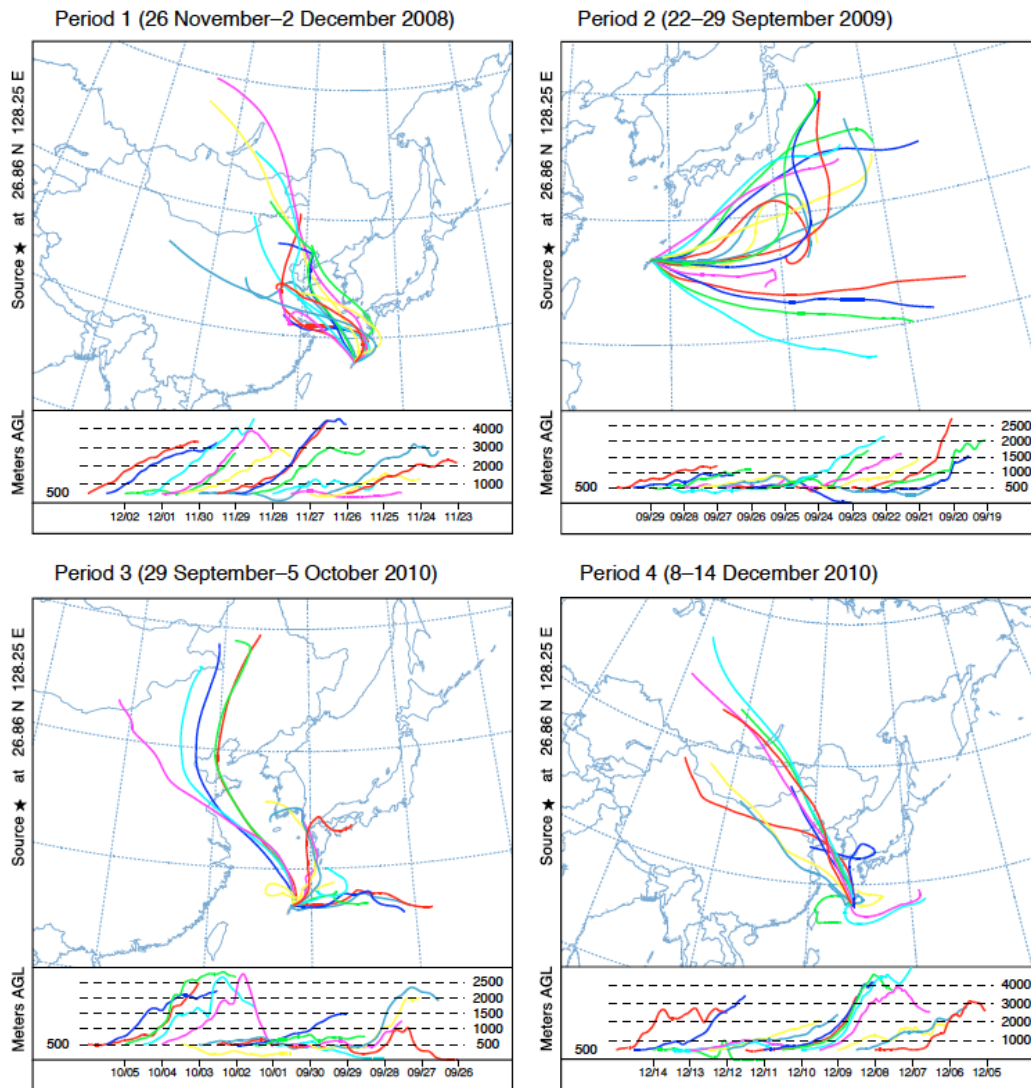


Figure 6 Backward trajectories of air masses during Periods 1–4 (November 26–December 2, 2008; September 22–29, 2009; September 29–October 5, 2010; and December 8–14, 2010) at Cape Hedo, starting at an altitude of 500 m for 72 h every 12 h (00:00 UT) through HYSPLIT vertical velocity model (Stein et al., 2015), using GDAS meteorological data (Stein et al., 2015; <http://ready.arl.noaa.gov/HYSPLIT.php>).

3.3 Evaluation of potential SCP sources during respective periods

As previously mentioned, the high SCP fluxes mostly occurred in autumn and winter when the air masses came from the northwest, i.e., northeastern parts of the Asian continent, suggesting that the high fluxes were presumably caused by the transportation of the SCPs emitted on the continent. Next, the source of the SCPs deposited at the study site is addressed using SCP elemental characteristics and sizes.

As shown in Figure 3 and 4, the SCP elemental characteristics and sizes during respective periods differ, although the results of the Mann–Whitney pairwise test show that the elemental characteristics between Periods 3 and 4 cannot be statistically differentiated from each other at least for the percentages of S. SCP elemental

compositions are generally different depending on their fuel type (i.e., coal, oil, or oil shale) (Rose et al., 1996; 1999b; Murakami-Kitase et al., 2010). The SCP compositions collected from East Asia vary among countries owing to the difference in primary fuel consumption in Japan, China, Korea, and Taiwan (Inoue et al., 2014). Inoue et al. (2014) showed that SCPs collected from Japan and South Korea have higher percentages of S than those from China and that the percentages of Si in the SCPs collected from China are slightly higher than those in SCPs from other countries. Because SCPs were chemically treated in the previous study to extract the particles from sediments, the elemental composition of the particles cannot be directly applied to the current study. However, we can refer to the elemental characteristics of SCPs found in respective countries to assess the source regions of the particles obtained in this study because Rose (1990) claimed that chemical extraction (HCl, HF, KOH, and H₂O₂ treatments) has no apparent effect on SCP elemental composition.

Although the size distribution of SCPs settling on a site depends on the original size of the emitted particles and many environmental factors (e.g., wind velocity, wind direction, and terrain topography), distance from the source has the possibility to critically influence the distribution (Larsen, 2003; Vukic et al., 2006; Inoue et al., 2013). Inoue et al. (2013) concluded that the SCP transportation mode possibly changes when the particle size is 10–20 µm; particles <10 µm tend to be transported over a distance longer than several tens of kilometers under favorable meteorological conditions whereas most of the particles >20 µm are generally deposited nearby or transported at most distances of tens of kilometers.

Thus, for the SCPs identified in this study, the difference in particle elemental compositions and sizes during respective periods indicates variations in their source regions during these periods. Based on the findings in previous studies and the results of our study, we discuss the possible SCP source regions during the respective periods identified in this study.

During Period 1, many of the particles are type C or D (Nos. 1–12), which are characterized by high percentages of Si and Al but low percentages of S relative to the other types. By referring to the SCP elemental characteristics in East Asian countries (Momose et al., 2012; Inoue et al., 2014), the elemental compositions of the particles (types C and D) during Period 1 are relatively similar to those of particles from China. The particle sizes during Period 1 are mostly less than 10 µm, implying that these particles could be transported over a long distance. This assumption is consistent with the fact that the dominant elements of fly ash particles collected from Chinese power plants are Si and Al (Zhang et al., 2005; Cao et al., 2008; Dai et al., 2010; 2014; Qi and Yuan, 2011). Furthermore, the trajectories during this period mostly pass over Northeast or East China (Figure 6). Thus, we

consider that many of the particles identified during Period 1 are from China.

All of the particles collected during Period 2 are assigned to type A (Nos. 1–12) which is characterized by high percentages of S. SCPs from Japan, South Korea, and Taiwan are abundant in S compared to those from China (Inoue et al., 2014), the particle elemental composition during Period 2 are relatively similar to those of particles from East Asian countries, not China. The particles during this period are characterized by their large sizes ($>20\ \mu\text{m}$), indicating that at least some particles were emitted from local sources. The trajectories during this period pass over the Pacific Ocean where no SCP occurs, except in Okinawa Island. Hence, we consider that all the particles during this period originated from Okinawa Island because their elemental compositions are nearly similar regardless of their size. The result indicates that these particles possibly originated from the same source or similar local sources.

During both Period 3 and 4, the SCPs have various elemental compositions and sizes. The sizes of the type C and D particles obtained during this period are generally small (less than $10\ \mu\text{m}$: Nos. 1–4 of Period 3 and Nos. 1–5, 7, and 8 of Period 4). Meanwhile, type A and B particles identified during these periods are mostly greater than or equal to $\sim 10\ \mu\text{m}$ in size (Nos. 5–13 of Period 3 and Nos. 5–13 of Period 4), some of which have a size greater than $20\ \mu\text{m}$ (No. 12 of Period 3 and No. 12 of Period 4). The air mass trajectories during these periods significantly varied depending on time, and the regions passed by the trajectories during Periods 3 and 4 are nearly similar to each other; the air masses passed over northeastern China and the Pacific Ocean.

We assume that most of the type C and D particles of small size originated from China because their elemental compositions and sizes are similar to the particle types found during Period 1. This assumption is consistent given that half of the air mass trajectories during the periods passed over northeastern China similar to those during Period 1. During Period 3 and 4, most of the type A particles of relatively large size presumably originated from local sources in Okinawa Island, because the particle elemental composition is similar to that of the particles of Period 2 and these particles tend not to be transported a long distance owing to their size. In addition, some of the trajectories during these periods are similar to those during Period 2. Thus, we assume that several other type A particles during Period 3 also were emitted from Okinawa Island similar to the large-sized type A particles. The possible source regions of the type B particles during Periods 3 and 4 are unclear. Considering the particle compositions and sizes, both the outside and inside of Okinawa Island could be potential source regions.

According to SCP elemental compositions and sizes, in the high SCP flux periods, such as Periods 1, 3, and 4,

the Asian-continent-derived particles were likely transported to the sampling site. This was also supported by the fact that most of the periods with high SCP fluxes occurred in autumn and winter when the air masses largely passed over the eastern Asian continent. In contrast, Period 2 showed low SCP flux, and the particle compositions and sizes indicated that most of the particles were emitted on the island when no air masses were passing over the Asian continent. These findings suggest that the high SCP fluxes that occasionally occurring in autumn and winter mainly resulted from the transportation of particles from the Asian continent to Okinawa Island. Additionally, the deposition of SCPs at the sampling site was usually low, and most of the particles were emitted on the island.

4. Conclusion

A temporal variation in the fluxes, elemental compositions and sizes of SCPs was found in data collected at Cape Hedo, the northernmost part of Okinawa Island, Japan. High SCP fluxes mostly occurred in periods when air masses came from the Asian continent in autumn and winter. In the periods with high SCP fluxes, some or most of the particles were characterized by their small sizes and similarity of composition to the particles that came from China. In contrast, in the periods with low SCP flux, the particles were larger in size and showed different elemental compositions compared with those from China. The results of this study show that on the northernmost part of Okinawa Island, in the sampling duration, SCP fluxes were relatively low, and the occasional high SCP fluxes resulted from the transportation of particles from the Asian continent to the sampling site.

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Supplementary information

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.apr.2019.11.011>.

S1 Sizes and proportions of the elements of SCPs in the samples collected during Periods 1–4 (sheets 1–4). Calculated SCP fluxes during the respective periods (sheet 5). Errors of the SCP fluxes obtained in this study were estimated from multiple counting number of the particles on the identical samples (sheet 6).

S2 Backward trajectories of air masses every two weeks in each month from October 2008 to January 2011, i.e., the sampling duration.

S3 *p* values obtained from Mann–Whitney pairwise test for the percentages of S of SCPs in the samples collected during Periods 1–4.

S4 Backward trajectories of air masses during the nine periods with high SCP fluxes.