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Deposition of long-range transported particulate matter on the needle surfaces of Japanese cypress (*Chamaecyparis obtusa*) grown in Nagasaki located in the western region of Japan

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Abstract

To characterize the deposition of long-range transported particulate matter (PM) on the foliar surface of Japanese forest trees, we periodically collected the PM deposited on the needle surface of mature Japanese cypress (*Chamaecyparis obtusa*) grown in the mountainous area of Nagasaki located in the western region of Japan from 24 April to 30 October, 2017. Metal element compositions and concentration ratios along with the ratios of Pb isotopes in the PM were analyzed. The total amount of metal elements (Na, Mg, Al, K, Ca, V, Cr, Mn, Fe, Ni, Cu, Zn, As and Pb) on the needle surfaces was relatively low during summer and autumn but was high during the spring when there was high atmospheric concentration of PM with diameter less than 2.5 μm due to influence of outflow from Asian continent. The seasonal variations in the amounts of less-abundant metal elements (Al, V, Ni, Cu, Zn, As and Pb) exhibited similar trends. The Pb amount varied with Zn amount at a constant ratio of 0.4, which was close to the Pb/Zn ratio of PM in China. Most of the Pb isotope ratios ($^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$) in the PM were close to those observed in the Chinese coal. Therefore, Pb on the needle could have originated from the coal combustion in China. The enrichment factor (EF) of Pb ranged from 650 to 2270, and was significantly correlated with the $^{207}Pb/^{206}Pb$ ratios, suggesting that components having EFs of greater than 650 could have originated from anthropogenic source. The amount of Pb significantly correlated with that of Ni, Cu, Zn, and As, which showed EFs more than 650. These results indicate that the long-range transported PM, including Pb, Ni, Cu, Zn, and As, originated from the anthropogenic sources in China, and deposited on the needle of *C. obtusa* grown in Nagasaki.

Key words: Back trajectory analysis, Enrichment factor, Long-range transport, Particulate matter deposition on forest, Pb isotope ratio

1. Introduction

Asian countries face the problem of air pollution that is caused by particulate matter (PM). In the eastern and southern regions of Asia, concentration of PM with the diameter less than 2.5 μm ($PM_{2.5}$) has increased during the period from 1998 to 2012 (Boys *et al*., 2014). The PM emissions mainly originate from China and India (Ohara *et al*., 2007; Lu *et al*., 2011) and cause high PM concentrations in the neighboring countries (Zhang and Cao, 2015; Mishra and Chaturvedi, 2017). In Japan, the air pollution caused by the long-range transported PM due to outflow from the Asian continent have been observed frequently during the winter and spring, especially in regions of western Japan such as the Kyushu area (Hidemori *et al*., 2014; Ikeda *et al*., 2014; Kaneyasu *et al*., 2014; Akimoto *et al*., 2015; Tatsuta *et al*., 2017). Because the deposition velocity of $PM_{2.5}$ is relatively low compared with coarse particles and gaseous pollutants such as ozone and SO_2, this PM can be transported over a long range (Colvile, 2002). However, the deposition velocity of $PM_{2.5}$ is observed to be relatively high in forests as compared with that in short vegetation (Fowler, 2002). Moreover, some recent dry deposition models predict dry deposition velocity over coniferous forest to be one order of magnitude higher than that over grass and water (Petroff *et al*., 2008; Khan and Perlinger, 2017). In Japan, because approximately 70% of the land is covered by forests, the majority of the long-range transported PM could deposit on the forest trees.

In western Japan, such as in the Kyushu area, the forest is dominated by evergreen forest tree species (Nakanishi *et al*., 1983), which has leaves or needles even in the season with transboundary air pollution. In Nagasaki, which is located in the northwestern part of the Kyushu area, the main plantation tree specie is Japanese cypress (*Chamaecyparis obtusa*), which is an evergreen coniferous tree species. It has been suggested that the deposition velocity of PM onto the foliar surface is higher in coniferous trees than that observed in case of broad-leaved trees because of complex structure of the shoots and the smaller leaves in conifers (Beckett *et al*., 2000: Freer-Smith *et al*., 2004; Hwang *et al*., 2011). Therefore, it is possible that the long-range transported PM, including $PM_{2.5}$, deposit onto the needles of *C. obtusa* grown in Nagasaki, Japan. However, there is insufficient information regarding PM deposition on Japanese forest trees to support this hypothesis (Fukazawa *et al*., 2012; Sase *et al*., 2012; Hara *et al*., 2014).

It has been reported that the PM is trapped in waxes coating the foliar surface (Dzierżanowski *et al*., 2011). On the other hand, the metal element composition and the ratios among these metal

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elements in the atmospheric PM has been used to identifying the source of the PM (Hidemori *et al*., 2014; Kaneyasu *et al*., 2014; Taniguchi *et al*., 2017; Shimada *et al*., 2017). Furthermore, the ratios between the isotopes of Pb observed in the PM can also be used to characterize the sources of the PM and to trace the long-range transportation of air pollutants (Mukai *et al*., 1994; Bollhöfer and Rosman, 2001; Komárek *et al*., 2008; Cheng and Hu, 2010). In the present study, the PM deposited on the surfaces of the needles of *C. obtusa* in Nagasaki was collected periodically. These samples were analyzed in terms of the metal element composition, the concentration ratios of the metal elements, and the Pb isotope ratios to characterize the deposition of long-range transported PM on the foliar surface of Japanese forest trees.

2. Materials and methods

2.1 Site description

The study site was located on the Nagaura Mountain in the Nishi-sonogi peninsula in Nagasaki (32.91N, 129.74E, 559 m a.s.l) at the western end of Japan. The site was dominated by Japanese cypress (*C. obtusa*), an evergreen coniferous tree species. Preliminary data on the mass concentration of $PM_{2.5}$ measured at the Yukinoura and Muramatsu monitoring stations, which were located close to the study site, was obtained from the Air Environment Early Warning System in Nagasaki (http://nagasaki-taiki.aa0.netvolante.jp/). At the monitoring stations, mass concentrations of $PM_{2.5}$ were measured by a beta-ray absorption method (FPM-377, DKK-TOA Corp. Japan). Because $PM_{2.5}$ can be transported over a longer range than PM including coarser particles, such as PM_{10} and suspended particulate matter (SPM), and could be one of indicators of transboundary air pollution, we obtained and showed the mass concentration of $PM_{2.5}$ in the present study.

2.2 Back-trajectory analysis

Back-trajectory analyses were conducted using the HYSPLIT4 model from the United States National Oceanic and Atmospheric Administration (NOAA) (Stein *et al*., 2015; Rolph *et al*., 2017). The initial altitude and the calculation time were set to 600 m and 48 h, respectively. Because the anthropogenic PM could only be transported within the atmospheric boundary layer, an isobaric analysis was selected to obtain average transport path in the boundary layer. Since the uncertainty of trajectories increases with transport time (Stohl *et al*., 2001) and isobaric trajectories are considered to be less accurate as compared with the 3-dimensional trajectories starting above the height of the Planetary Boundary Layer, the total run time of the back-trajectory analysis was set to be 48 h. As shown in the results and discussion section, the resulting trajectories are sufficient to analyze flow patterns at the observation site. SO_2 emission data in 2000 was obtained from the Regional Emission inventory in ASia (REAS) 1.11 (http://www.jamstec.go.jp/frsgc/research/d4/emission.htm) (Ohara *et al*., 2007).

2.3 Sampling of *C. obtusa* needle

The *C. obtusa* is main tree species planted in the study site. Three mature trees of 10−15 m in height were targeted to perform needle harvesting. Samplings were conducted on 24 April, 8 and 22 May, 13 June, 3 and 31 July, 30 August, 26 September and 30 October in 2017. One- and two-year old needles were sampled from the three different parts of the canopy of each tree, so that a total of nine samples were collected. The dry weight of the harvested needles in each of the samples ranged from approximately 4 to 10 g. The samples were analyzed to obtain the amount of PM deposited on needle surfaces and metal element composition of this PM.

2.4 Extraction of epicuticular wax and PMs deposited on the needle surfaces

The harvested needles were initially washed using 150 mL of ultrapure water for 3 min to eliminate the debris and were then dried in an oven (LC-124, ESPEC, Japan) at 40°C. The dried needles were then washed using 150 mL of chloroform for 20 s. It has been reported that the PM is trapped in waxes (Dzierżanowski *et al*., 2011). Because the plant cuticle, which coats the foliar surface and its outer layer comprises epicuticular wax, is hydrophobic (Bargel *et al*., 2006; Samuels *et al*., 2008), hydrophobic PM, including metal elements, adhere to it. In this study, chloroform was used to quickly dissolve and extract the epicuticular wax, as has been done since the 1980s (e.g. Cape *et al*., 1989; Turunen *et al*., 1997; Takamatsu *et al*., 2001; Dzierżanowski *et al*., 2011). The PM from the wax was thus suspended in the chloroform. The PM was then collected on quartz fiber filters (QR-100, Advantec MFS, Inc., Japan) by gravitational filtration and was subsequently collected on polytetrafluoroethylene (PTFE) membrane filters with a pore size of 0.1 μm (Omnipore™ Membrane filters JVWP, Merck Millipore Ltd., Ireland) by vacuum filtration. After washing with chloroform, the needles were dried under normal atmospheric conditions, and the projected needle area was measured using an portable area meter (LI-3000A, LI-COR, Lincoln, NE, USA). The filtrated chloroform was then evaporated, and the residual wax was determined gravimetrically (Sase *et al*., 1998). The amount of wax was expressed as that on needle surface area ($g\ m^{-2}$). The needle surface area was obtained by multiplying the projected needle area by two.

2.5 Metal element compositions and Pb isotope ratio of the PM samples from the needle surfaces

The quartz fiber and PTFE filters used to collect the PM from needle surfaces were digested in a solution containing with 3 mL hydrofluoric acid (48% HF, Ultrapur-100, Kanto Chemical Co., Inc., Japan), 6 mL nitric acid (61% HNO_3 for EL, Kanto Chemical Co., Inc., Japan), and 1 mL hydrogen peroxide (30.0−35.5% H_2O_2 for atomic absorption spectrometry, Kanto Chemical Co., Inc., Japan) using a microwave digestion system (START D, MILESTONE S.r.l., Italy). The PTFE vessels of the digestion system were sealed and heated with a gradual increase in temperature to reach a temperature of 180ºC for 20 min. The amounts of the following elements were measured: Na, Mg, Al, K, Ca, V, Cr, Mn, Fe, Ni, Cu, Zn, As, and Pb. The amounts of V, Cr, Mn, Ni, Cu, Zn, As, and Pb were measured using an inductively coupled plasma-mass spectrometer (ICP-MS, P-5000, Hitachi, Ltd., Japan). The isotopic ratio of Pb was calculated from the concentrations of ^{206}Pb, ^{207}Pb, and ^{208}Pb measured by

the ICP-MS using the Lead Isotopic Standard Solution (NMIJ CRM 3681-a No. 021, National Institute of Advanced Industrial Science and Technology, Japan). To measure the amounts of Na, Mg, Al, K, Ca, and Fe, an inductively coupled plasma optical emission spectrometer (ULTIMA2, HORIBA, Japan) was used. The concentration of each element was calculated by subtracting a blank value from the measured value. The blank values were obtained using the quartz fiber and PTFE filters through which pure chloroform was flowed with the same procedure that was used to collect the PM from the needle surfaces. The amount of total and each metal elements on the needle surface was expressed in the form of metal elements amount, which were sum of the amount on the quartz and PTFE filters, per unit needle surface area.

2.6 Calculation of the enrichment factor (EF)

The enrichment factor (EF) can be used to evaluate the relative contributions of crustal and non-crustal (i.e., anthropogenic) sources of aerosol particles (Zoller *et al*., 1974). The EF for PM is usually calculated using the following equation:

$$EF = ([X]_{aeroso1}/[Al]_{aerosol})/([X]_{crust}/[Al]_{crust})$$

where $[X]_{aerosol}$ and $[X]_{crust}$ are the concentrations of the target element (X) in the aerosol and the crust, respectively, and $[Al]_{aerosol}$ and $[Al]_{crust}$ are the concentrations of Al in the aerosol and the crust, respectively. This analysis was applied to the PM deposited on the surfaces of *C. obtusa* needle by calculating the EF values according to the following equation:

$$EF = ([X]_{NS}/[Al]_{NS})/([X]_{crust}/[Al]_{crust})$$

where $[X]_{NS}$ and $[Al]_{NS}$ are the concentrations of the target element (X) and Al, respectively, in the PM deposited on the needle surfaces. The $[X]_{crust}/[Al]_{crust}$ ratio was calculated using the data reported by Taylor and McLennan (1995).

3. Results and discussion

Seasonal variation in the daily mean mass concentration of $PM_{2.5}$ on average for the two monitoring stations near the study site is depicted in Fig. 1. High concentrations of $PM_{2.5}$ close to or exceeding the daily mean concentration of 35 μg m^{-3} specified in the Environmental Quality Standards for the $PM_{2.5}$ in Japan was observed on 29 and 30 April as well as 8 May. From 29 April 0800 local time (LT) to 30 April 1300 LT, the hourly mean $PM_{2.5}$ concentrations were consistently observed to be greater than 30 μg m^{-3}. Back-trajectories during this period depicted in Fig. 2a suggest that the air mass reached the site from northern China. At 0900 LT 30 April, when the hourly mean $PM_{2.5}$ concentration reached a maximum of 42 μg m^{-3} during this period, transport from high SO_2 emission area in Shandong and Jiangsu, China was suggested. From 8 May 0800 LT to 9 May 0000 LT, the hourly mean concentrations were close to or greater than 40 μg m^{-3} and reached a maximum of 60 μg m^{-3} at 1800 LT 8 May. During this period, the back-trajectory analyses depicted in Fig. 2b suggest that the air mass consistently reached the study site from Shandong. In these back-trajectory analyses, we confirmed that there was no rainfall at the study site and on the pathway from the continent to the site, except for at 0100 LT 9 May at 0.5 mm h^{-1} at the site. Kaneyasu *et al*. (2014) reported that the $PM_{2.5}$ concentration in northern part of the Kyushu region of Japan, including Nagasaki, was dominated by the inflow of long-range transported aerosols, even in large city such as Fukuoka. The present study site is located to the west of Fukuoka and is closer to the Asian continent. These results suggest that the high concentration of $PM_{2.5}$ at the study site could be due to the outflow from the Asian continent, where the high concentrations of PM have been observed (Zhang and Cao, 2015). On the other hand, during summer, such a consistently high concentration of $PM_{2.5}$ of greater than 30 μg m^{-3} was rarely observed, and the daily average concentration was ranged from 4 to 23 μg m^{-3} (Fig. 1). The density plots of the back trajectories in Fig. 3 suggest that the movement of air masses from the Asian continent to the observation site occurs rarely during this period.

Fig. 4 shows the seasonal variation in the total amount of metal elements (Na, Mg, Al, K, Ca, V, Cr, Mn, Fe, Ni, Cu, Zn, As, and Pb) deposited on the surfaces of the needles of *C. obtusa* grown in mountainous area of Nagasaki. Large amounts of the metal elements were deposited during the spring, when high $PM_{2.5}$ concentrations were observed. Thereafter, the amount of metal elements on the needle was lower during the summer and autumn seasons. The most abundant components in the PM were Na, Mg, K, Ca, and Fe, which either accounted for approximately or more than 10% (Table 1). Seasonal variations in the amount of each major element deposited on the needles were almost similar to the variations in the total metal elements. The seasonal variations in the amounts of less-abundant metal elements that were deposited on the needles, which accounted for less than 1% of the total amount of metal elements, are presented in Fig. 5. The amount of Mn did not exhibit any

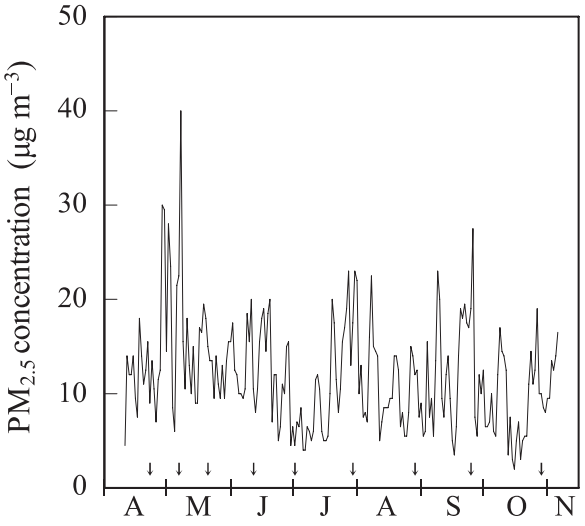

Fig. 1. Daily mean mass concentration of particulate matter with the diameter less than 2.5 μm ($PM_{2.5}$) during 2017 measured at the Yukinoura and Muramatsu monitoring stations, which were located close to the present study site (the Nagasaki Prefectural Forest Park). The data were obtained from the Air Environment Early Warning System in Nagasaki. The arrows indicate the dates on which *C. obtusa* needles were sampled to characterize the particulate matter deposited on the surfaces of the needles.

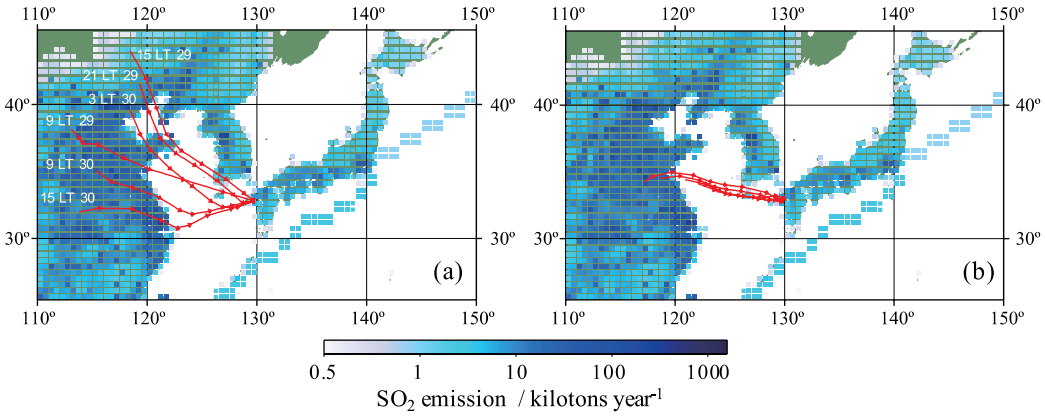

Fig. 2. 48-hr isobaric backward trajectories starting from observation site at 600 m above ground level for the high $PM_{2.5}$ concentration periods (a) from 29 April 0900 LT to 30 April 1500 LT, 2017 and (b) from 8 May 0900 LT to 9 May 0300 LT, 2017. Time interval of each trajectory line is 6-hr. Arrows are for 6-hr increments. Emissions in 2000 are from REAS1.11.

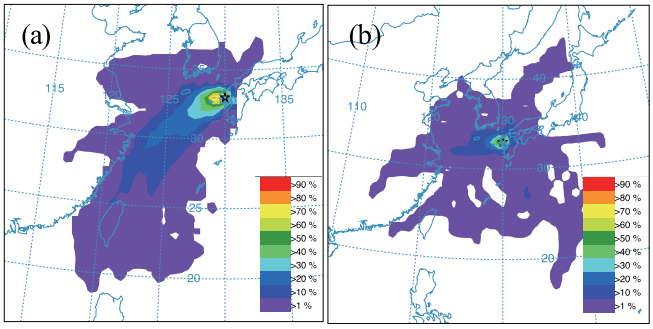

Fig. 3. Density plots of the 48-hr back trajectories at 600 m above ground level terminating at the present study site during the period from (a) 3 to 31 July and (b) 31 July to 30 August, 2017. Percentage of number of trajectories passing through each grid square per number of trajectories were indicated in the color.

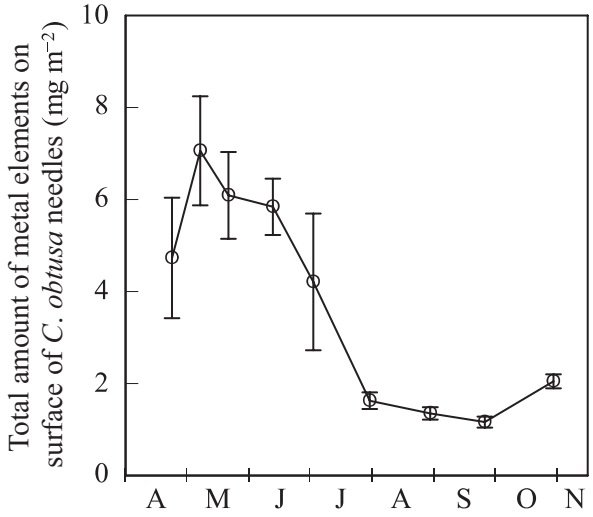

Fig. 4. Seasonal variation in the total amount of metal elements in the particulate matter deposited on the surfaces of *C. obtusa* needles in 2017. Each value represents the mean of the values collected from three trees, and error bars represent the standard deviations in these values. The annual mean value was 3.79 mg m^{-2}.

significant seasonal variations. On the other hand, Cr was identified on the needles during both summer and autumn but was not identified during the spring. In contrast, the deposition amounts of Al, V, Ni, Cu, Zn, As, and Pb were high during the spring and decreased through the summer, which was similar to the trends observed in the total amount of metal elements and the individual amounts of the relatively abundant metal elements.

Because it has been suggested that the PM is trapped in waxes on the surface of leaves or needles (e.g., Dzierżanowski *et al.*, 2011), we measured seasonal variation in the amount of wax on the surface of *C. obtusa* needles (Fig. 6). Although the seasonal variation was nonsignificant, the amount of wax tended to be high during the spring, and to be low during the summer. Furthermore, there was a significant positive linear relationship between the amount of wax and that of metal elements on the needle surface ($R = 0.799$, $p < 0.01$). During the spring, therefore, high amount of wax and the high concentration of $PM_{2.5}$, which could be caused by PM from the Asian continent, could cause the increased deposition of the metal elements on the needle surface of *C. obtusa* grown in Nagasaki. Because the metal elements of PM on the needle surface could derive from not only fine particle but also coarse particle, the high $PM_{2.5}$ concentration could not directly cause the increased amount of metal elements on the needle surface. However, the high $PM_{2.5}$ concentration suggest high deposition of PM on the needle surface because the concentration of SPM, which includes coarser particle than $PM_{2.5}$, had similar seasonal trend and significantly correlated with $PM_{2.5}$ concentration throughout the present study period (data not shown). On the other hand, the decrease in the amounts of metal elements during the summer could be due to low $PM_{2.5}$ concentration, decreased amount of wax and the washing the elements off from the needle surface by precipitation during rainy season, which is typically during the early summer in Japan.

The ratios of metal elements in the aerosol, such as Pb/Zn ratio, has been used to distinguish the source region of the aerosol (e.g., Kaneyasu *et al.*, 2014). The amounts of Pb was plotted against those of Zn deposited on the surfaces of *C. obtusa* needles (Fig. 7). The slope of the regression line indicates that

Table 1. Seasonal variations in the amounts of most abundant elements (mg m^{-2}) in the particulate matter deposited on the surfaces of *C. obtusa* needles in 2017.

Date	Na	Mg	K	Ca	Fe
24 Apr.	0.40 (0.11)	0.54 (0.16)	0.89 (0.24)	0.80 (0.29)	2.01 (0.52)
8 May	0.62 (0.10)	0.84 (0.16)	1.47 (0.13)	0.93 (0.24)	3.25 (0.63)
22 May	0.55 (0.06)	0.72 (0.09)	1.18 (0.22)	0.63 (0.07)	2.96 (0.44)
13 Jun.	0.58 (0.07)	0.67 (0.07)	1.14 (0.04)	0.54 (0.06)	2.80 (0.38)
3 Jul.	0.37 (0.13)	0.45 (0.15)	0.78 (0.32)	0.54 (0.06)	1.98 (0.89)
31 Jul.	0.24 (0.05)	0.15 (0.02)	0.27 (0.03)	0.31 (0.02)	0.60 (0.14)
30 Aug.	0.10 (0.02)	0.12 (0.02)	0.23 (0.04)	0.27 (0.05)	0.58 (0.11)
26 Sep.	0.08 (0.01)	0.11 (0.01)	0.20 (0.03)	0.30 (0.16)	0.44 (0.08)
30 Oct.	0.16 (0.02)	0.21 (0.02)	0.30 (0.04)	0.40 (0.12)	0.92 (0.10)
Mean	0.35	0.42	0.72	0.52	1.73
% of total amount	9.2	11.2	18.9	13.8	45.6

Each value represents the mean of the values collected from three trees, and the standard deviation of these values is illustrated in the parentheses. Mean: annual mean amount. %: percentage of the mean of each element relative to the annual mean of total amount of metal elements indicated in the legend of Fig. 4.

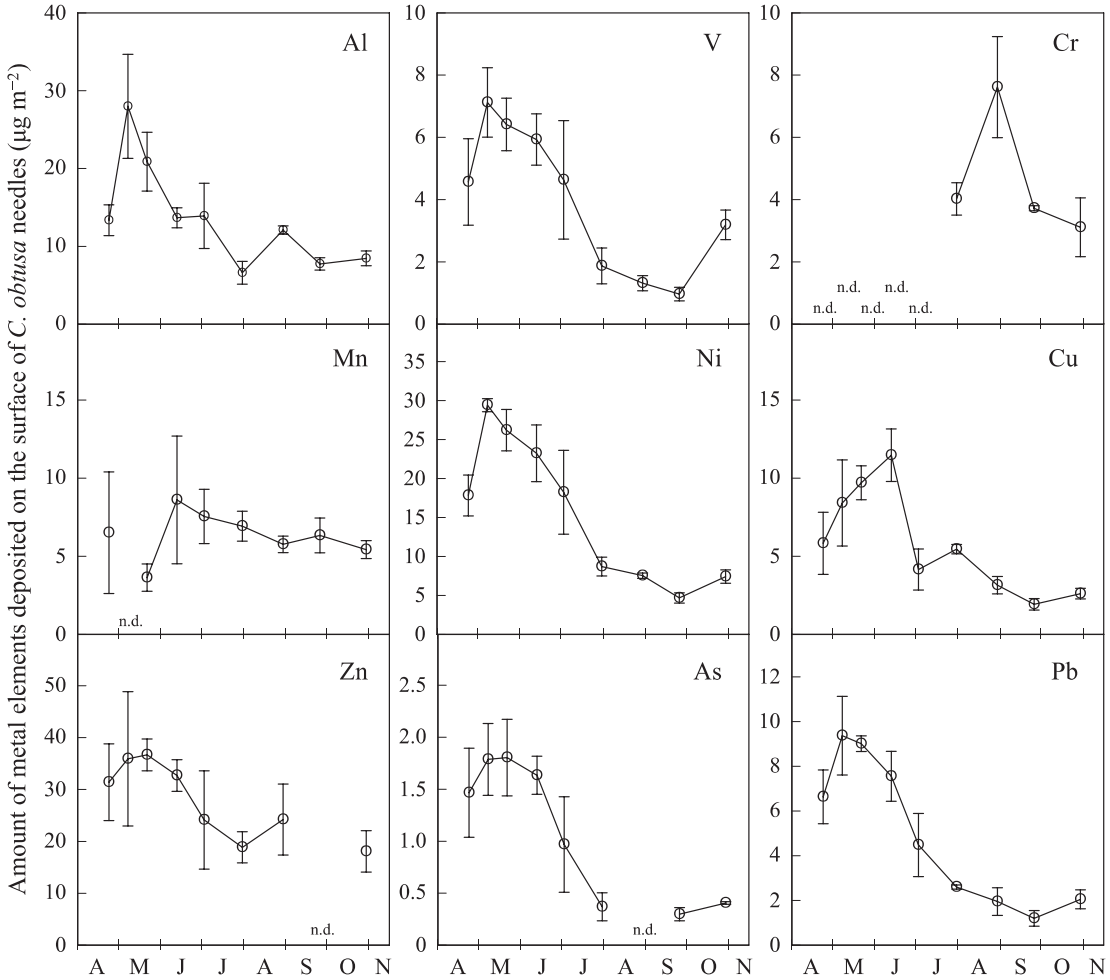

Fig. 5. Seasonal variations in the amounts of Al, V, Cr, Mn, Ni, Cu, Zn, As, and Pb in the particulate matter deposited on the surfaces of *C. obtusa* needles in 2017. Each value represents the mean of the values collected from three trees, and error bars represent the standard deviations in these values. n.d.: more than one-third of the values were below the detection limit of ICP-MS.

the amount of Pb on the needles varied in concurrent with the changes in the amount of Zn at a ratio of 0.4. This ratio was closer to that observed in Beijing, China (0.43) and differed from that observed in Tokyo, Japan (0.29) (Okuda *et al*., 2013). These results suggest that the changes in Pb and Zn amounts on the needle surface could be caused by deposition, dropping out

with decreased wax and washing off of long-range transported particulate matter from China.

The ratios of Pb isotopes in PM have been used to identify its origins (Bollhöfer and Rosman, 2001; Komárek *et al*., 2008; Cheng and Hu, 2010). Mukai *et al*. (1994) reported that the use of the ratios of Pb isotope along with back-trajectory analysis enabled reliable analysis of the long-range transport of air pollutants in Japan. Fig. 8 presents the relationship between the

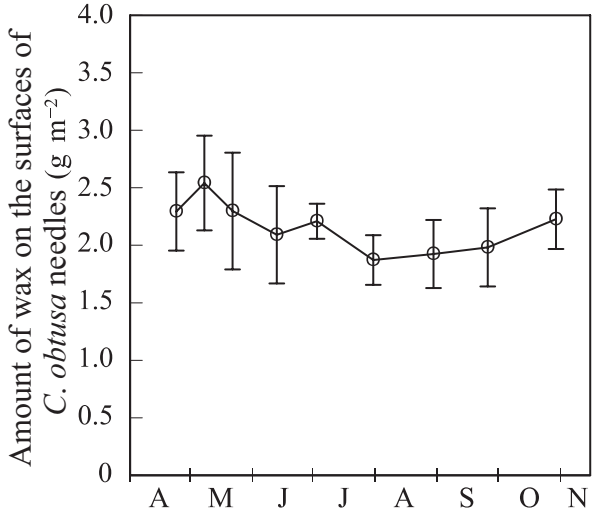

Fig. 6. Seasonal variation in the amount of wax on the surfaces of *C. obtusa* needles in 2017. Each value represents the mean of the values collected from three trees, and error bars represent the standard deviations in these values.

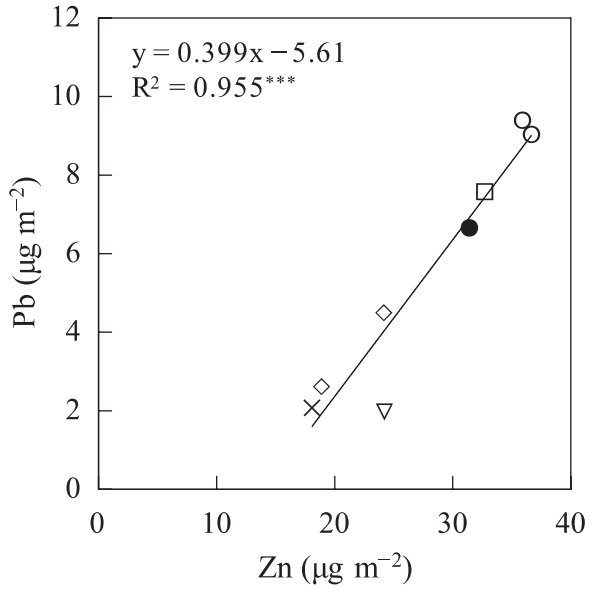

Fig. 7. Relationship between the amounts of Pb and Zn deposited on the surfaces of *C. obtusa* needles. ●: April, ○: May, □: June, ◇: July, ▽: August, ×: October. Each value represents the mean of the values collected from three trees. Data obtained in September was not plotted, because the amount of Zn was not detected. The solid line that indicates the regression line and the corresponding R^2 value are represented in the figure (*** $p < 0.001$).

$^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ ratios in the PM that was deposited on the needle surfaces. Hu *et al*. (2015) reported that the $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ in Chinese coal were in the ranges of 0.850−0.876 and 2.07−2.16, respectively. In the present study, the $^{208}Pb/^{206}Pb$ ratio was within the range of that observed in Chinese coal, except during September, when the least amount of Pb was deposited (Figs. 5 and 8). On the other hand, Mukai *et al*. (2001) reported that $^{207}Pb/^{206}Pb$ ratios in northern Chinese lead ore was in the range of 0.875−0.930. In the present study, $^{207}Pb/^{206}Pb$ ratio was within the range observed in Chinese coal and lead ore from April to July, when the large amount of Pb were deposited (Fig. 8). Hidemori *et al*. (2014) indicated that the Pb in the $PM_{2.5}$ collected at Nagasaki originated from coal combustion in China. Furthermore, the back-trajectory analysis during the period with high $PM_{2.5}$ concentration at the study site revealed that the air masses reached the study site from northern China, where the emission and atmospheric concentration of Pb were high (e.g., Zhengzhou: 34.76N, 113.65E) (Tian *et al*., 2012; Duan and Tan, 2013) (Fig. 2). These results indicate that the Pb in the PM deposited on the needle surfaces of *C. obtusa* in Nagasaki could have originated from the coal combustion in northern China.

The enrichment factor (EF) has been used to distinguish between the natural and anthropogenic sources of atmospheric PM (Zoller *et al*., 1974; Okuda *et al*., 2008; Yuan *et al*., 2008; Shimada *et al*., 2017). The EF of Pb ranged from 650 to 2270 (Table 2). Because uncertainty has been pointed out regarding the accuracy of the use of EF to distinguish between the PM sources (Reimann and de Caritat, 2005), the EF of Pb was plotted against the $^{207}Pb/^{206}Pb$ ratio (Fig. 9). The EF of Pb exhibited significant positive relationship with $^{207}Pb/^{206}Pb$ ratio. Because the Pb deposited on the needle surfaces could be considered to originate

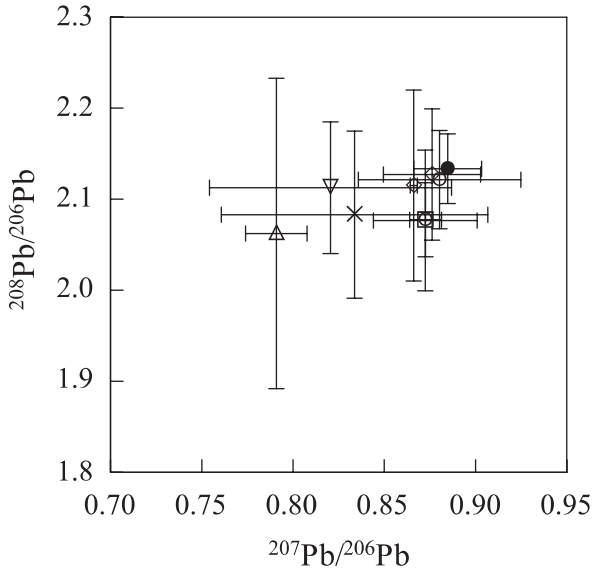

Fig. 8. Relationship between $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ ratios in the particulate matter deposited on the surfaces of *C. obtusa* needles. ●: April, ○: May, □: June, ◇: July, ▽: August, △: September, ×: October. Each value represents the mean of the values collected from three trees, and the vertical and horizontal bars represent the standard deviations.

from combustion processes in the northern China, we assumed that the source of the metal elements with EFs of greater than 650 was anthropogenic. The EFs of Cr, Ni, Cu, Zn, and As were all observed to be greater than 650 (Table 2), suggesting these metal elements could have originated from an anthropogenic source. On the other hand, the EFs of the most abundant metal components on the needle surfaces were all observed to be less than 650 (data not presented). Because these elements are present in the continental crust in the order of % (Taylor and McLennan, 1995), the major elements could be derived from natural sources, such as Asian dust, which typically reaches Japan during the spring (Kurosaki and Mikami, 2003).

To clarify the location of the anthropogenic source from which the less-abundant metal elements on the needles have originated,

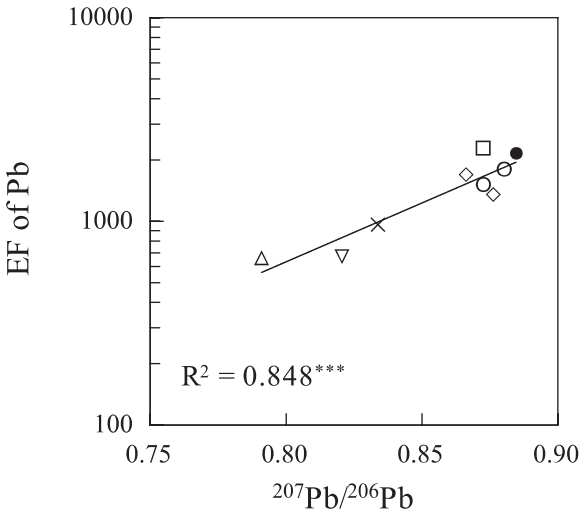

Fig. 9. Relationship of the enrichment factor (EF) of Pb with $^{207}Pb/^{206}Pb$ ratio in the particulate matter deposited on the surfaces of *C. obtusa* needles. ●: April, ○: May, □: June, ◇: July, ▽: August, △: September, ×: October. Each value represents the mean of the values collected from three trees. Linear regression analysis was conducted using the correlations of the logarithm of EF with $^{207}Pb/^{206}Pb$ ratio. The solid line that indicates the regression line and the corresponding R^2 value are represented in the figure (*** $p < 0.001$).

the amount of Pb originating from coal combustion in northern China was compared with the amounts of Cr, Ni, Cu, Zn, and As, which depicted EFs of greater than the 650 over time (Table 3). There was no significant correlation between Pb and Cr, which was observed on the needles during the summer when the concentration of $PM_{2.5}$ was not high (Figs. 1 and 4). During the summer, the air masses from the Asian continent rarely reached the study site (Fig. 3). The port of Nagasaki as well as the factories around the port are located to the south of the study site. Although sufficient information was not available about PM emission from the factories and ships around the port, the observed Cr may have originated from these domestic sources. However, the amount of Pb depicted significant positive correlations with the amounts of Ni, Cu, Zn, and As, suggesting that these metal elements were emitted and/or transported in similar manners. Duan and Tan (2013) reported that the concentrations of these metal elements in the atmospheric PM were high in several cities located in northern China (Ni and Zn in Shijiazhuang: 38.04N, 114.48E; Cu in Tianjin: 39.14N, 117.18E; As in Zhenzhou: 34.76N, 113.65E and Yinchuan: 38.47N, 106.27E). These results indicate that the long-range transported PM, including Pb, Ni, Cu, Zn, and As, that was deposited on the needles of *C. obtusa* in Nagasaki originated from northern China. In the western region of Japan, such as Nagasaki, while many researchers have indicated the long-range transport of PM from Asian continent (e.g., Kaneyasu *et al*., 2014; Hidemori *et al*., 2014), present study further indicates issue of the long-range transported PM for the Japanese forest trees.

4. Conclusions

In the present study, we periodically measured the amount and metal element compositions of PM deposited on the needle surfaces of mature *C. obtusa* grown in the mountainous area of Nagasaki from 24 April to 30 October, 2017. The total amount of metal elements on the needle surfaces was high during the spring when there was high atmospheric concentration of $PM_{2.5}$ due to influence of outflow from Asian continent. The Pb amount varied with Zn amount at a constant ratio of 0.4, which was close to the Pb/Zn ratio of PM in China. Most of the Pb isotope ratios ($^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$) in the PM were close to those observed in the Chinese coal. The amount of Pb significantly correlated with that of Ni, Cu, Zn, and As. These results indicate

Table 2. Seasonal changes in the enrichment factor (EF, $\times 10^3$) of less-abundant metal elements in the particulate matter deposited on the surfaces of *C. obtusa* needles in 2017.

Date	V	Cr	Mn	Ni	Cu	Zn	As	Pb
24 Apr.	0.49 (0.19)	n.a.	0.07 (0.04)	5.66 (1.52)	1.54 (0.68)	2.81 (0.94)	6.40 (2.30)	2.14 (0.59)
8 May	0.37 (0.13)	n.a.	0.00 (0.00)	4.48 (1.19)	1.08 (0.62)	1.54 (0.63)	3.78 (1.56)	1.50 (0.63)
22 May	0.42 (0.03)	n.a.	0.02 (0.01)	5.10 (0.42)	1.53 (0.21)	2.05 (0.35)	4.66 (0.08)	1.78 (0.26)
13 Jun.	0.59 (0.12)	n.a.	0.09 (0.05)	6.98 (1.48)	2.77 (0.64)	2.80 (0.61)	6.52 (1.24)	2.27 (0.48)
3 Jul.	0.45 (0.04)	n.a.	0.10 (0.03)	5.53 (0.16)	1.00 (0.03)	2.09 (0.27)	3.75 (0.22)	1.35 (0.11)
31 Jul.	0.38 (0.05)	1.66 (0.12)	0.15 (0.01)	5.52 (0.43)	2.85 (0.64)	3.38 (0.93)	2.71 (0.47)	1.69 (0.24)
30 Aug.	0.15 (0.02)	1.50 (0.38)	0.07 (0.02)	2.55 (0.10)	0.86 (0.09)	2.40 (0.66)	n.a.	0.67 (0.18)
26 Sep.	0.18 (0.05)	1.18 (0.04)	0.11 (0.02)	2.60 (0.46)	0.83 (0.19)	n.a.	2.29 (0.82)	0.65 (0.23)
30 Oct.	0.49 (0.03)	0.97 (0.26)	0.09 (0.01)	3.51 (0.24)	0.94 (0.10)	2.55 (0.80)	2.48 (0.49)	0.95 (0.17)

Each value represents the mean of the values collected from three trees, and the standard deviation of these values is illustrated in the parentheses. n.a.: the EF value was not assessed because more than one-third of the values were below the detection limit of ICP-MS.

Table 3. Correlations of the amount of Pb with the amounts of Cr, Ni, Cu, Zn, and As deposited on the surfaces of *C. obtusa* needles.

Cr	Ni	Cu	Zn	As
$0.038^{n.s.}$ (n=4)	0.982*** (n=9)	0.878** (n=9)	0.955*** (n=8)	0.988*** (n=8)

Pearson's correlation test: $^{**}p < 0.01$, $^{***}p < 0.001$, n.s. = not significant. The number of plots that was used for each analysis is indicated in the parentheses.

that the long-range transported PM, including Pb, Ni, Cu, Zn, and As, originated from the anthropogenic sources in China deposited on the needle of *C. obtusa* grown in Nagasaki located in the western region of Japan.

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