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Measurement of Ambient PAHs in Kumamoto: Differentiating Local and Transboundary Air Pollution

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ABSTRACT

We developed an index to investigate the effect of transboundary air pollution (TAP) on the air quality of Kumamoto City, Japan. We estimated the effect of TAP by using the index and positive matrix factorization (PMF). Polycyclic aromatic hydrocarbons (PAHs) and trace metals were analyzed from the daily samples of the Total Suspended Particles (TSPs) collected seasonally from Oct. 2014 to Aug. 2015. These chemical components exhibited high concentrations in spring and winter, which is consistent with the data in the literature. Pb was identified as the TAP tracer owing to its high concentrations in winter and spring. Indeno(1, 2, 3-cd)pyrene (IcdP) was used as the local emission tracer in Kumamoto on the basis of previous studies. We applied the IcdP/Pb ratio as the index. The index enables the detection of TAP in daily data sets. PMF identified six factors: soil and road dust, biomass and waste burning, heavy oil combustion, fishing boats, vehicle emission, and coal combustion. The average contribution of TAP on the days when transboundary pollution was high was evaluated as being 46%.

Keywords: Indeno(1, 2, 3-cd)pyrene; Lead; Contribution of transboundary air pollution; Contribution of local air pollution; PMF analysis.

INTRODUCTION

In Japan, transboundary air pollution (TAP) caused by particulate matter less than or equal to 2.5 μm in aerodynamic diameter ($PM_{2.5}$) is frequently reported by the media. Metallic elements, ionic compounds, and organic compounds are the major chemical components of $PM_{2.5}$. Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous organic components of $PM_{2.5}$. PAHs are mainly caused by the incomplete combustion of fossil fuels, but also originate from natural sources such as forest fires (Cheruyiot *et al*., 2015). Some PAHs such as BaP are carcinogenic, mutagenic and endocrine disruptors (Hayakawa, 2016). Therefore, we believe that TAP caused by PAHs might present health risks for the population of Japan. To determine the increase in risk caused by TAP, the contribution of TAP to the air quality in Japan must be evaluated.

Numerous studies conducted in Japan (Kaneyasu and Takada, 2004; Tang *et al.*, 2005; Ogawa *et al.*, 2012; Sato *et al.*, 2013) reported that PAHs were transported from China to Japan. Kaneyasu and Takada (2004) collected fine atmospheric aerosols from Miyako Island and Amami Island and analyzed their chemical components. They observed high PAH concentrations in winter. In addition, the black carbon (BC) concentration exhibited a strong positive correlation with PAH concentration. This result suggests that PAHs are transported together with BC from China in winter. Ogawa *et al*. (2012) reported that the total suspended particle (TSP) and total PAH concentrations in Fukue Island (a remote site) were the highest in the air masses from China. Sato *et*

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al. (2013) reported that PAHs observed in Fukuoka City and Fukue Island mainly were originated from coal or biomass combustion in spring or winter, whereas they were originated from petroleum combustion and coal and biomass combustion in summer.

However, no study has attempted to evaluate the quantitative contribution of PAHs from TAP using a receptor model. Sato *et al.* (2013) indicated that 65%–75% of the total PAHs in Fukuoka City are transported by comparing the daily data of PAHs in Fukuoka with those of Fukue Island. However, Sato *et al.* (2013) assumed that all PAHs in Fukue Island were transported from China.

In the present study, we developed an index to investigate the contribution of TAP to the air quality in Kumamoto, Japan. To develop the index for differentiating TAP from local pollution, we divided the concentration of a local pollution tracer by the concentration of a transboundary pollution tracer. The resultant ratio decreases when transboundary pollution arrives in Kumamoto and increases when local pollution is high.

Indeno(1, 2, 3-cd)pyrene (IcdP) was selected as the local pollution tracer and Pb was used as the transboundary pollution tracer. According to a report by the Tokyo Metropolitan Government (2011), vehicle emission and waste burning are the main sources of $PM_{2.5}$ in Tokyo. The government study created data sets for a chemical mass balance model to identify the contribution of $PM_{2.5}$ sources. Taniguchi *et al*. (2017) demonstrated that Pb was a transboundary pollution tracer in Kumamoto.

Finally, by using this index and positive matrix factorization (PMF) analysis, we undertook the first evaluation of the contribution of TAP caused by PAHs on the basis of measurement data to be conducted in Japan.

METHODS

Aerosol Sampling

Measurements were taken in Kumamoto city in autumn (October 14–21, 2014), winter (December 17–21, 2014), spring (March 13–17, 2015), and summer (July 27–August 2, 2015). The measurement site was at the top of a nine-story building in Kumamoto University in Kumamoto City. Kumamoto City is located on Kyushu Island in southwestern Japan and is approximately 900 km from Shanghai. Kumamoto has 740,000 inhabitants (2014 data) and only light and service industries are located in the city. Thus, the sampling site is not affected by any nearby heavy industrial point sources, making it a favorable location for observing the arrival of TAP. The monitoring site was located in the eastern part of the city and can be classified as an urban background site, which is influenced to some extent by road traffic emissions from a city center arterial road 1400 m to the west and a minor (although frequently congested) two-lane road crossing the university area (Moreno *et al*., 2013).

TSPs were collected on a quartz fiber filter (QR-100, Advantec, Tokyo, Japan) using a high-volume air sampler (HV-1000F, Sibata, Tokyo, Japan) for 24 h. The flow rate of the sampler was 1 m^3 min^{-1}. Before sampling, quartz fiber filters were heated at 773 K for 4 h to remove any organic contaminants. The TSP concentration was determined using the difference between the weight of the filter measured before and after the sampling.

Aerosol Sample Pretreatment

Each sample filter was spiked with a 100-μL isooctane solution containing a mixture of naphthalene-d8, anthracene-d10, p-terphenyl-d14, and benz(a)anthracene-d12 (5 ppm each) as a surrogate for the evaluation of PAH recovery. Subsequently, the filter sample was cut into approximately 2 × 0.5 cm pieces. These filter pieces were sonicated in 50–70 mL of dichloromethane three times and then sonicated in 60 mL of methanol two times to extract organic materials. Each sonication lasted 20 min. All dichloromethane and methanol extracts were mixed in a 300-mL flask and concentrated to approximately 3 mL at a pressure of 213–533 hPa at 305 K in a rotary evaporator (Model R-205, Büchi Corporation, Flawil, Switzerland). Insoluble particles were removed from the concentrated extract by using a Teflon syringe filter (ISOLUTE SPE Glass filtration 6 mL, Biotage AB, Uppsala, Sweden). The filtered extract was then placed in a 20-mL amber glass vial and was reconcentrated to near dryness under a gentle stream of dry nitrogen gas. Subsequently, the reconcentrated extract was dissolved in 1.0 mL of *n*-hexane. The *n*-hexane solution of each aerosol sample was fractionated into five polarity fractions by using a flash chromatograph (Isolute VacMaster-10, Biotage AB, Uppsala, Sweden). The molecules in the sample were separated into five fractions by using (i) hexane (15 mL), (ii) hexane/toluene (5.6:9.4, 15 mL), (iii) hexane/dichloromethane (1:1, 15 mL), (iv) hexane/ethyl acetate (2:3, 20 mL), and (v) formic acid/methanol (4:96, 20 mL) as eluents. PAHs were included in the first fraction of the *n*-hexane eluent. This fraction was placed in a 1.5-mL amber glass vial and concentrated to near dryness under a gentle stream of nitrogen gas. As internal standards for the evaluation of PAHs signal intensities, a 100-μL isooctane solution containing a mixture of acenaphthene-d10 and chrysene-d12 (5 ppm each) was added to the 1.5-mL vial containing the concentrated sample. This solution was used for the PAH analysis.

GC/MS Analysis of Aerosol Samples

Each pretreated sample was analyzed using gas chromatography/mass spectrometry (GC/MS). A 1-μL aliquot of analytical sample was injected into a GC/MS instrument (6890N GC instrument combined with 5973 Network Mass Selective Detector, Agilent Technologies, Palo Alto, CA, USA) in the splitless mode. The temperature of the injection port was 583 K. The injected sample was separated by a capillary column (Agilent J&W HP-5MS; length = 30 m, diameter = 250 μm, film thickness = 0.25 μm, Agilent Technologies, Palo Alto, CA, USA). Helium was used as the carrier gas. The flow rate of the carrier gas was 1.0 mL min^{-1}. The column temperature was maintained at 343 K for 2 min, increased to 423 K at 30 K min^{-1}, then to 583 K at 4 K min^{-1}, and finally maintained at 583 K for 10 min. The separated samples were introduced into the mass spectrometer and were ionized using electron ionization. A total of 15 PAHs with 3–7 rings were monitored using the selected-ion

monitor method: phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benz(a)anthracene (BaA), chrysene (CHR), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(e)pyrene (BeP), benzo(a)pyrene (BaP), indeno(1,2,3-cd)pyrene (IcdP), dibenz(a,h)anthracene (DahA), benzo(ghi)perylene (BghiP), coronen (COR), and retene (RET). The quantified results for the PAHs were corrected by considering the recoveries determined using internal surrogate standards. The mean recoveries of samples were anthracene-d10 80% (67–100%), p-terphenyl-d14 106% (94–121%), and benz[a]anthracene-d12 109% (86–141%). In this study, 2–3 field blank samples, which were treated in a manner similar to the aerosol samples but were not used for aerosol sampling, were prepared during each observation period. No PAH contamination was detected in any of these blank filters. In our method, the detection limit was 0.006–20.989 ng.

Positive Matrix Factorization

PMF is a factor analysis technique based on a weighted least-squares fit and the error estimates of the measured data (Paatero and Tapper, 1994). The USEPA PMF version 5.0 was used to analyze the input data matrix of 304 samples (Table 1) and 32 columns species (Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Sn, Sb, Ba, Pb Bi, FLT, PYR, BaA, CHR, BbF, BkF, BeP, BaP, IcdP, BghiP, DahA, COR, RET, and $PM_{2.5}$). Data from the Cape Hedo Atmosphere and Aerosol Monitoring Station (CHAAMS), Fukue, and the Fukuoka site, which were analyzed in our laboratory, were included in the PMF analysis (Table 1). In addition, data of the site on Tuoji Island in China, which were obtained simultaneously with our experiments through collaborative research, were included in the PMF to determine the effect of TAP. The CHAAMS, Fukue, Fukuoka, and Tuoji sites have been described in detail by Shimada *et al*. (2015), Sato *et al*. (2013), and Zhang *et al*. (2016). The sampling method for $PM_{2.5}$ and analytical method for $PM_{2.5}$ and metals were reported by Shimada *et al*. (2015). The error fraction was set to 0.15. An additional uncertainty of 13% was added to each value. In this study, to identify the source categories through PMF analysis, we first determined 1) the optimal number of factors and 2) the stability and uncertainty of the solution. Thus, we evaluated the results of 1) base runs and 2) a bootstrap run and displacement approach (DISP). For missing values, the median of these components was used, and their errors were estimated at four times the species-specific median. If the concentration was less than or equal to the detection limit, the uncertainty was calculated as 5–6 times the detection limit (USEPA, 2014). Subsequently, the signal-to-noise (S/N) ratio for all data was examined to ascertain whether the measurement variability was real or within the noise level (USEPA, 2014); species with S/N ratios greater than 1 were considered to be "strong." All species except $PM_{2.5}$ were set as "strong." $PM_{2.5}$ was set as the total variable.

To determine the optimal number of factors, various numbers of factors should be tested and the PMF calculation results then evaluated (Bhanuprasad *et al.*, 2008; Kitayama *et al.*, 2009). We performed 100 random runs and retained the runs that produced minimum Q values for 3–10 factors in base runs. A six-factor solution was selected based on the most physically interpretable results with the least factor smearing and most normal residuals.

To estimate the stability and uncertainty in factor contributions, we performed a bootstrap model analysis and DISP. Tables 2 and 3 present the summary of the bootstrap analysis and DISP, respectively. Bootstrap analysis was performed 20 times with a minimum correlation value R = 0.6. The average percentage of bootstrap factors mapped back to the original PMF factors of this study was 94% (83%–100%; Table 2), which was higher than that of Callén *et al*., 2013 (average was 79%; 74%–90%). This indicated that our factor profile solutions were sufficiently unique. No swaps were present in all factors for dQmax 4 and 8 (Table 3). Thus, the solution was stable. These error estimations demonstrated that the model simulation results were acceptable.

Table 1. Sample information of each site.

Site	Sampling Year and Month (number of days)	Characteristics of the Site
CHAAMS	2010 January (3), March (7), April (14), October (2), December (11) 2012 March (8), April (7), October (6), December (6), 2013 April (7), October (6), December (5), 2014 April (5), October (5), 2015 March (5)	remote site
Kumamoto	2014 October (8), December (5), 2015 March (5), July and August (7)	urban site
Tokyo	2014 December (5), 2015 March(5), July and August (6)	urban site
Fukue	2010 March (7), April (15), October (5), December (14) 2011 March (6), April (6), November (9) 2012 March (10), October (4) 2013 February and March (12), October (6) December (5)	remote site
Fukuoka	2010 March (7), April (14), December (15) 2012 March (11)	urban site
Tuoji	2012 October (9), December (10)	remote site

Table 2. Percentage of bootstrap factors mapped back to the original PMF factors from the six-factor PMF solution.

Boot Factor	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Unmapped	% Bootstrap factors mapped to original PMF factors
1	100	0	0	0	0	0	0	100%
2	0	91	3	0	0	3	3	91%
3	3	0	92	1	1	1	2	92%
4	6	0	4	83	4	1	2	83%
5	0	0	0	0	99	1	0	99%
6	0	0	0	0	0	100	0	100%

Table 3. Swaps according to factors in DISP.

	Factor1	Factor2	Factor3	Factor4	Factor5	Factor6
dQmax = 4	0	0	0	0	0	0
dQmax = 8	0	0	0	0	0	0

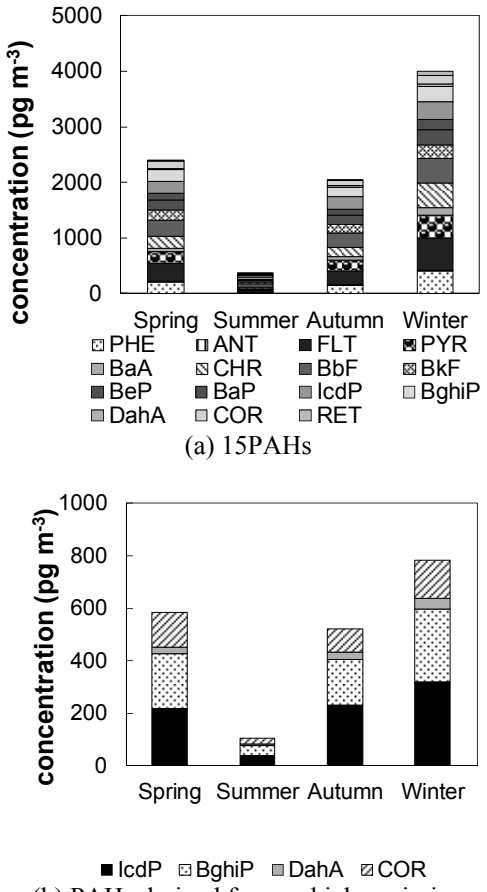
RESULTS AND DISCUSSION

Seasonal Variation of PAH and Element Tracer Concentrations between Transboundary and Local Air Pollution in Kumamoto

Fig. 1 presents the seasonal variation in the (a) 15 PAHs and (b) PAHs from vehicle emission (Ravindra *et al*., 2008) in Kumamoto. The PAH concentration was highest in winter and the lowest in summer (Fig. 1(a, b)). The seasonal pattern of the PAH concentration observed in Kumamoto was similar to that of the ambient PAH concentrations reported in previous studies in East Asia (Tang *et al*., 2005; Sato *et al.*, 2008; Ma *et al*., 2010; Yang *et al.*, 2017). The lowest concentration was observed in summer, which is attributed to 1) the 3–4-ring PAHs exhibiting high volatility in summer and 2) photochemical degradation occurring because of the high intensity of solar light and high concentration of ozone (Tang *et al*., 2005). In winter, the PAH concentration increased because PAHs produced by the burning of fossil fuels for heating are transported from China (Tang *et al.*, 2005). Furthermore, low temperature increases PAH concentrations because of PAHs partitioning to the particle phase and decreasing atmospheric reaction (Li *et al.*, 2009; Liu *et al*., 2016).

Vehicle emission and waste incineration are some of the main sources of $PM_{2.5}$ in Tokyo (Tokyo Metropolitan Government, 2011). According to Taniguchi *et al.* (2017), vehicle emission is the main source of $PM_{2.5}$ in Kumamoto. IcdP is known as a vehicle emission tracer (Ravindra *et al.*, 2008). PAHs from vehicle emission can be an indicator of local pollution because they have the highest concentration of IcdP in Kumamoto. Thus, IcdP was appropriate for use as the local pollution tracer.

Pb was selected as the transboundary pollution tracer. Coal combustion is increasing in China (Kurokawa *et al.*, 2013) and is one of the largest sources of $PM_{2.5}$ in Beijing (Huang *et al.*, 2014; Lang *et al.*, 2017). In Kumamoto, no coal combustion source was observed near the sampling site. Thus, the coal combustion tracer can be considered as a transboundary pollution tracer (Taniguchi *et al.*, 2017). PAH concentration is affected by dispersion, deposition, and photochemical degradation, whereas the concentration of metallic elements is affected only by dispersion and deposition. Hence, metal components are more appropriate transboundary pollution tracers than are PAHs because the concentration of metal components does not decrease through chemical reactions during transport. Fig. 2 presents the seasonal variation in (a) anthropogenic metals and (b) metals from coal combustion (Waheed *et al.*, 2011)



(a) 15PAHs

(b) PAHs derived from vehicle emission

Fig. 1. Seasonal variation in (a) 15 PAHs and (b) PAHs from vehicle emission.

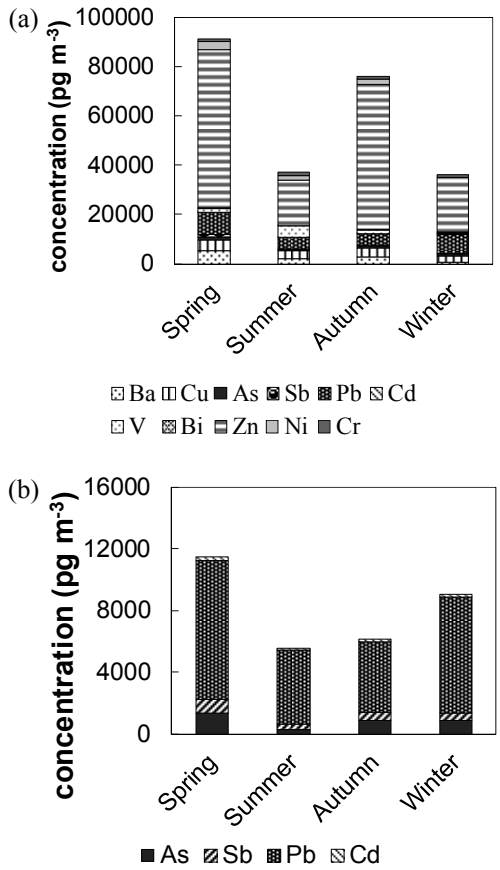


Fig. 2. Seasonal variation in (a) anthropogenic metals and (b) metals from coal combustion.

in Kumamoto. The concentration of anthropogenic metals was higher in autumn and winter (Fig. 2(a)). This indicates that anthropogenic metals are affected by local pollution. By contrast, the seasonal variation in elements from coal combustion in Kumamoto was high in spring and winter and low in summer and autumn. This result is consistent with that in CHAAMS (Shimada *et al*., 2015). This indicates that the seasonal variation in metals from coal combustion is affected by transboundary pollution. Furthermore, Taniguchi *et al.* (2017) report that Pb is a useful tracer for identifying TAP in Kumamoto. Metals from coal combustion had the highest Pb concentration. Thus, Pb is appropriate to be used as a transboundary pollution tracer.

In conclusion, the IcdP/Pb ratio is the most promising candidate for the index. The usefulness of the IcdP/Pb ratio is discussed in the following sections.

Development of the Index for Differentiating Transboundary Air Pollution from Local Pollution

The applicability of the IcdP/Pb ratio can be confirmed using two methods. One method is to compare the IcdP/Pb ratio between transboundary pollution and local pollution which were differentiated by weather conditions, simulation model results, and the diagnostic ratio of PAHs. Another method is to compare the IcdP/Pb ratios of this study with those in the relevant literature. A detailed description of the confirmation process follows.

First, we compared daily IcdP/Pb values with the results of differentiation between transboundary pollution and local pollution in terms of weather conditions, simulation model results, and the diagnostic ratio of PAHs. To determine meteorological conditions, weather maps from the Japan Meteorological Agency (http://www.data.jma.go.jp/fcd/yoho/hibiten/) were examined. For example, the weather maps of Kumamoto on October 15–17, 2014 indicate transboundary and local pollution (Fig. 3). The arrival of transboundary pollution corresponds with air masses moving from China to Japan. For the model analysis, back trajectory and SPRINTARS (http://sprintars.riam.kyushu-u.ac.jp/; Takemura *et al.*, 2000, 2002, 2005) were used.

Fig. 4 presents the back trajectories on October 15 and 16 combined with the SPRINTARS results. The back trajectory data indicate that an air mass travelled from China on October 16 (Fig. 4(b)). In addition, SPRINTARS confirmed that sulfate aerosols were transported from China. In some cases, the differentiation between transboundary and local air pollution is difficult to achieve based only on back trajectory analysis.

Fig. 5 presents the PAH and anthropogenic metal fractions on October 15 and 16, which were determined as being

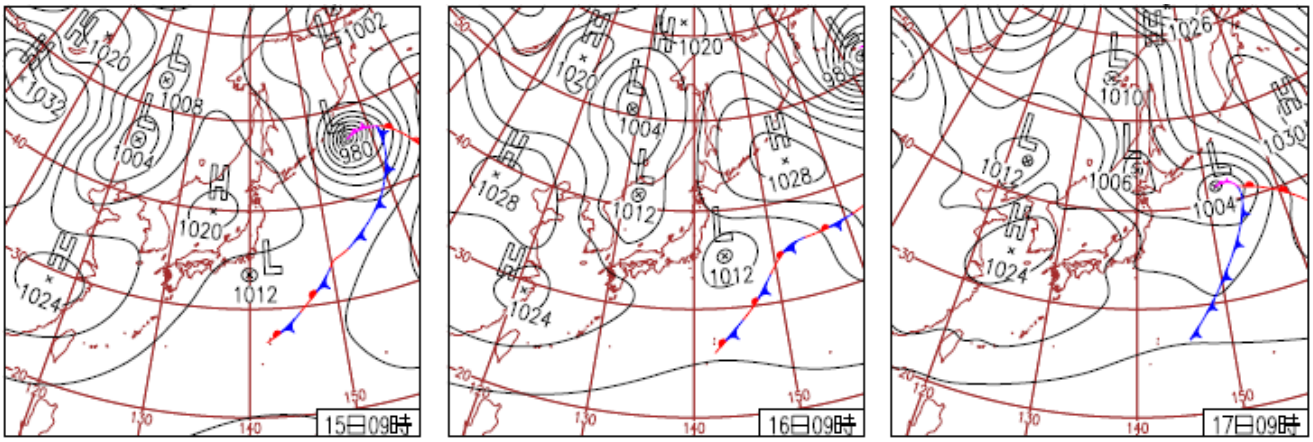


Fig. 3. Weather maps of the arrival day of transboundary air pollution and the day when local pollution was intense. Left: 9 am JST, Oct. 15; middle: 9 am JST, Oct. 16; right: 9 am JST, Oct. 17.

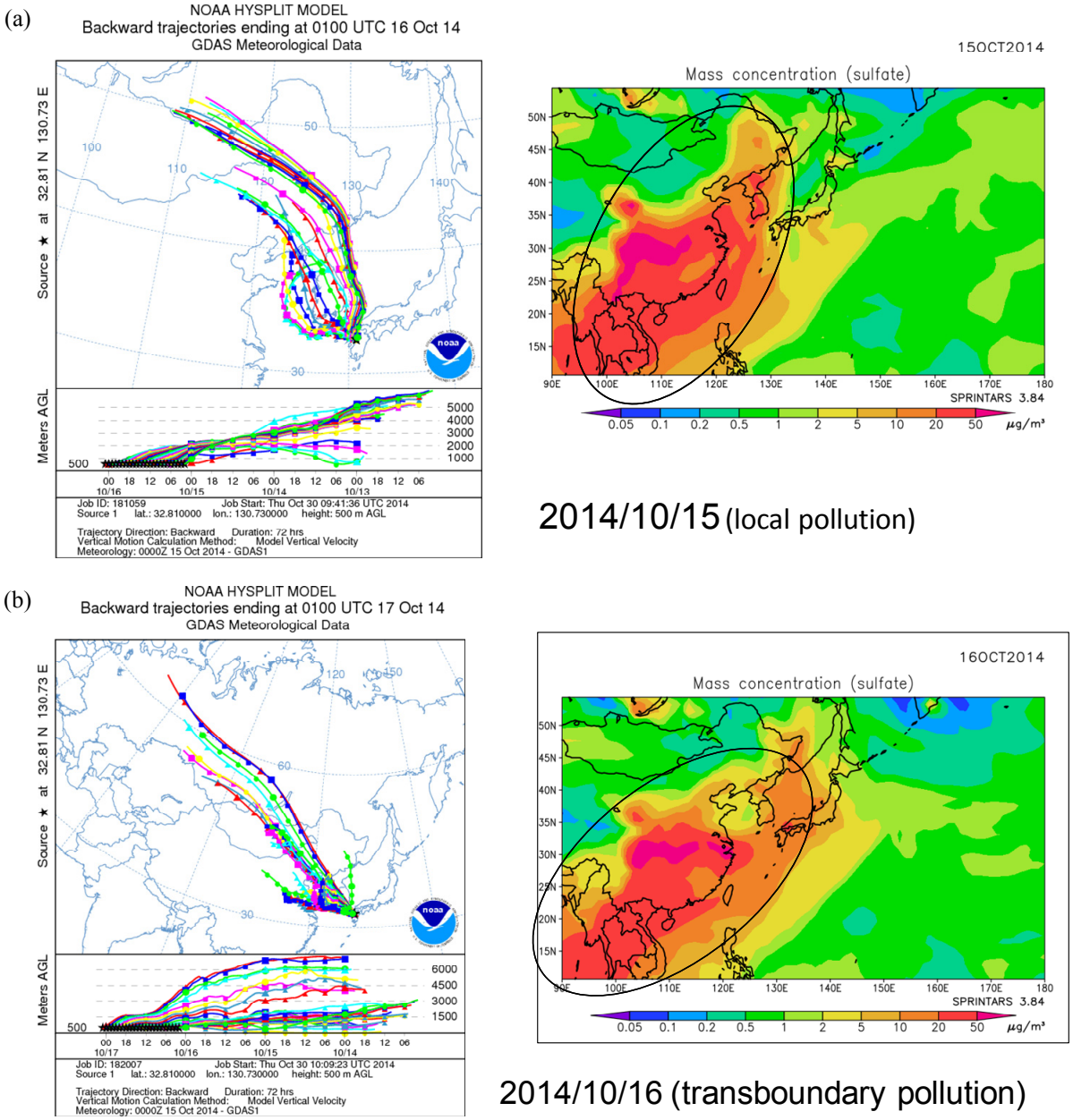


Fig. 4. Back trajectory and SPRINTARS of (a) the arrival day of transboundary air pollution and (b) the day when local pollution was intense in Kumamoto.

either transboundary pollution or local pollution. When local pollution was dominant, high-molecular weight PAH concentrations were high (Fig. 5(a)). When the transboundary pollution was dominant, the concentrations of elements derived from coal combustion (Pb, As and Cd) were high (Fig. 5(b)). These results suggest that the main source of local pollution was vehicle emission, and the main source of transboundary pollution was coal combustion. To obtain the diagnostic ratio of PAHs, BaP/BeP and BaA/CHR ratios were used. Both ratios are indexes of aging (Callén *et al.*, 2011; Lv *et al.*, 2016). Table 4 presents the daily BaP/BeP and BaA/CHR ratios in Kumamoto. Low ratios indicate that the air masses are aged because BaP and BaA decompose faster than BeP and CHR in the atmosphere. This indicates the arrival of TAP in Kumamoto. Compared with the BaP/BeP and BaA/CHR ratios on October 15, these ratios were lower on October 16.

Fig. 6 presents the daily variation in IcdP/Pb with the results of differentiation by model, meteorological data, and the diagnostic ratio of PAHs in Kumamoto. Except in the summer season, the IcdP/Pb ratio was low when transboundary pollution arrived and high when local pollution was dominant. In the summer season, the IcdP/Pb ratio was always low. This is possibly because IcdP was decomposed by atmospheric reactions caused by the high intensity of sunlight and high temperature. Thus, the IcdP/Pb ratio can be used to differentiate between TAP and local pollution, except in the summer season, when it is invalid.

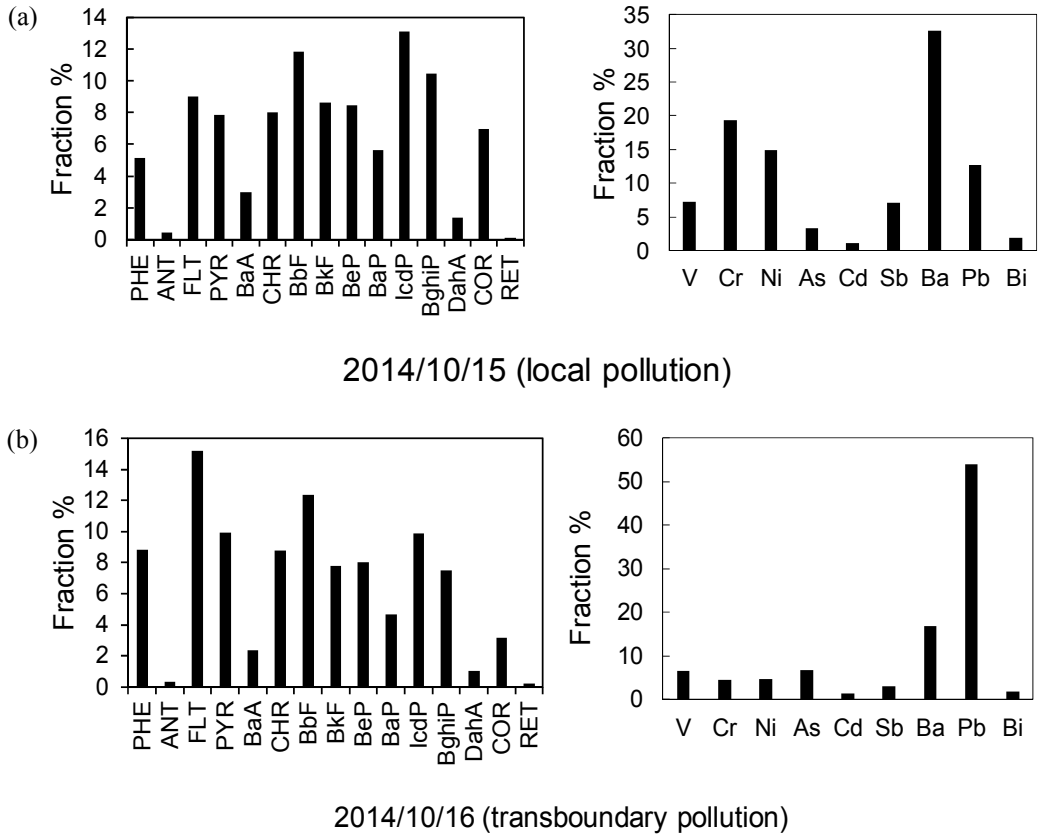


Fig. 5. Fractions of PAHs and anthropogenic metals on (a) the arrival day of transboundary pollution and (b) the day when local pollution was intense in Kumamoto.

Table 4. BaA/Chr and BaP/BeP ratios in Kumamoto.

	BaP/BeP	BaA/CHR
10/14/14	0.79	0.49
10/15/14	0.67	0.38
10/16/14	0.58	0.27
10/17/14	0.62	0.28
10/18/14	0.76	0.38
10/19/14	0.5	0.31
10/20/14	0.49	0.34
10/21/14	0.42	0.3
12/17/14	0.7	0.37
12/18/14	0.78	0.42
12/19/14	0.7	0.35
12/20/14	0.7	0.31
12/21/14	0.63	0.31
03/13/15	0.53	0.2
03/14/15	0.56	0.24
03/15/15	0.62	0.36
03/16/15	0.67	0.35
03/17/15	0.58	0.29
07/27/15	0.53	0.31
07/28/15	0.48	0.3
07/29/15	0.39	0.26
07/30/15	0.57	0.34
07/31/15	0.48	0.36
08/1/15	0.46	0.37
08/2/15	0.41	0.37

Secondly, to confirm the applicability of IcdP/Pb for evaluating the threshold value between local pollution and transboundary pollution, we evaluated the IcdP/Pb reported in the literature (Deng *et al.*, 2006; Moon *et al.*, 2008; Table 5) and the data obtained at CHAAMS and in Tokyo. Deng *et al.* (2006) conducted sampling at Guiyu, an e-waste recycling area in China. In Guiyu, local air pollution is abnormally high because the emission source is near the sampling site. Thus, the IcdP/Pb ratio in Guiyu reflects local pollution. By contrast, Moon *et al.* (2008) conducted an observation at Gosan, a remote area on Jeju Island in Korea. This area is heavily affected by TAP from China (Moon *et al.*, 2008). Thus, the low IcdP/Pb ratio in Gosan reflects TAP. The IcdP/Pb ratio in Table 5 indicates that the IcdP/Pb ratio was low at Gosan.

To confirm the applicability of the IcdP/Pb ratio in Japan, we evaluated the IcdP/Pb ratio in Tokyo and CHAAMS. The sampling site in Tokyo is located in the suburban area and is far from China. Thus, we assumed that local pollution produces a greater contribution to pollution in Tokyo than it does in western Japan. CHAAMS has few significant emission sources in its vicinity, and is closer to China than Tokyo. Thus, CHAAMS receives a large quantity of transboundary pollution from China. For calculation, the summer data in Tokyo were used because the effect of TAP was the least in summer among the four seasons (Miura *et al.*, 2016). For the same reason, winter, autumn, and spring data from CHAAMS were used for the evaluation (Table 5).

Table 5. IcdP/Pb ratios in Guiyu, Gosan, CHAAMS, and Tokyo calculated using the average concentration of IcdP and Pb.

Site	IcdP/Pb	Literature
Guiyu (e-waste recycling site)	0.077	Deng *et al.*, 2006
Gosan	0.016	Moon *et al.*, 2008
Kumamoto 2014–2015 autumn winter spring	0.038	this study
CHAAMS 2014–2015 autumn spring	0.004	this study
Tokyo (Tama) summer	0.054	this study

A high IcdP/Pb ratio in Tokyo and low IcdP/Pb ratio in CHAAMS were evaluated. The IcdP/Pb ratio in Kumamoto was an approximately intermediate value between the ratio in CHAAMS and that in Tokyo. This indicates that transboundary pollution is linked with local air pollution in Kumamoto. The IcdP/Pb ratio in Tokyo in summer was about 0.05 (Table 5). In summer, local pollution in Tokyo is high because the city is mostly covered by the Pacific high pressure in summer and, consequently, TAP does not reach it. However, the IcdP/Pb ratio decreases because of the photochemical degradation of IcdP. Thus, the IcdP/Pb ratio in Tokyo in summer can be considered as the minimum value of local pollution. Moreover, the minimum value of IcdP/Pb on days when local pollution had a large effect was 0.067 (excluding summer data), whereas the maximum value of IcdP/Pb on days when TAP had a large effect was 0.039 (Fig. 6). The average of the maximum and minimum values was evaluated to determine the threshold value between local pollution and transboundary pollution. The average of the two values was 0.053, which is nearly the same as the IcdP/Pb ratio in Tokyo in summer. Therefore, we determined that the threshold value between local pollution and transboundary pollution was 0.05. Thus, the applicability of the IcdP/Pb ratio was confirmed using data from the literature and other sampling sites.

Estimation of the Contribution of Transboundary Air Pollution in Kumamoto by Using PMF and the Developed Index

Fig. 7 presents the factor profiles of the six identified factors. Those factors were identified mainly according to tracer distributions as follows: (1) fishing boats, (2) heavy oil combustion, (3) vehicle emission, (4) biomass and waste burning, (5) soil and road dust, and (6) coal combustion.

(1) The fishing boat factor was indicated by the high loading of Flu, Pyr, BaP, and IcdP (Lin *et al*., 2006) and the low loading of metallic elements. The emission of metallic elements from fishing boats is less than that from vehicles because fishing boats do not employ tires or brake pads.
(2) The heavy oil combustion factor was characterized by the high loading of V and Ni, which are tracers of heavy oil combustion on ships (Moldanová *et al.*, 2009).
(3) The vehicle emission factor was characterized by the high loading of Cu, Zn, Sn, and high-molecular PAHs such as IcdP, DahA, and COR. The high loading of Cu, Sn, and Ba is attributed to brake pad abrasion (Gietl *et al.*, 2010; Harrison, 2012). Zn is an indicator of motor oil additives (Pio *et al.*, 2013). High-molecular PAHs such as IcdP, COR, and DahA are tracers of gasoline vehicle emission (Miguel *et al.*, 1998; Zechmeister *et al.*, 2006).
(4) The biomass burning factor was characterized by the high loading of RET. RET is a tracer of biomass burning (Ramdahl, 1983).
(5) The soil and road dust factor was characterized by the high loading of Al, Fe, and Ba. Al and Fe are tracers of soil. The high loading of Ba is attributed to brake pad abrasion (Gietl *et al.*, 2010; Harrison *et al.*, 2012).
(6) The coal combustion factor was indicated by a high percentage of As, Cd, Sb, and Pb, which are tracers of coal combustion (Waheed *et al.*, 2011). The low loading of PAHs indicated that the air mass containing pollutants from coal combustion was transported across a long range because PAHs are reduced by the atmospheric chemical reactions during transport.

Coal combustion, heavy oil combustion, and fishing boats can be considered as transboundary pollution factors because these sources are outside Kumamoto City (Fig. 7). Soil and road dust, and biomass and waste burning can be considered as factors of both transboundary and local air pollution because they are common to both Japan and China. Moreover, according to Taniguchi *et al*. (2017), the contribution of biomass and waste burning is high in local air pollution in Kumamoto. Vehicle emission was considered as a factor of only local pollution because PAHs exhibited a high contribution in this factor profile. If this factor included transboundary pollution, the contribution of PAHs would be lower because of photochemical degradation during transport. Thus, Eq. (1) is used to calculate the contribution of transboundary pollution on the days when TAP arrived in Kumamoto.

$$Cont = (C_{transboundary} - C_{local\ BB\ and\ SD})/C_{all} \quad (1)$$

where *Cont* is the contribution of transboundary pollution on a day when transboundary pollution is intense,

$C_{transboundary}$ is the contribution of coal combustion, heavy oil combustion, biomass burning, fishing boats, and soil and dust on the days when the IcdP/Pb ratio is less than 0.05, $C_{local\ BB\ and\ SD}$ is the average contribution of biomass and soil and dust on the days when the IcdP/Pb ratio is more than 0.05, and C_{all} is the contribution of all factors on the days when the IcdP/Pb ratio is less than 0.05.

The average contribution of TAP on the days when transboundary pollution was dominant was 46 ± 9%

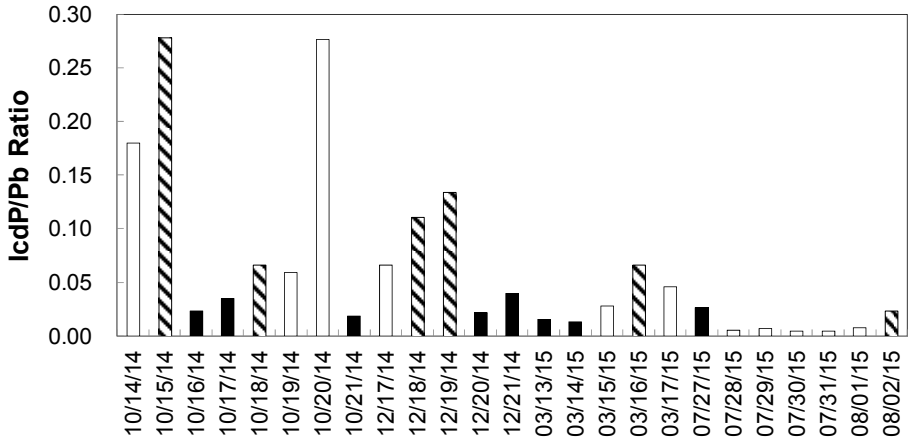


Fig. 6. Daily variation in the IcdP/Pb ratio with the results of differentiation by model, meteorological data, and diagnostic ratio of PAHs in Kumamoto. Black bar: transboundary pollution arrival; oblique lined bar: local pollution was dominant; white bar: unable to differentiate.

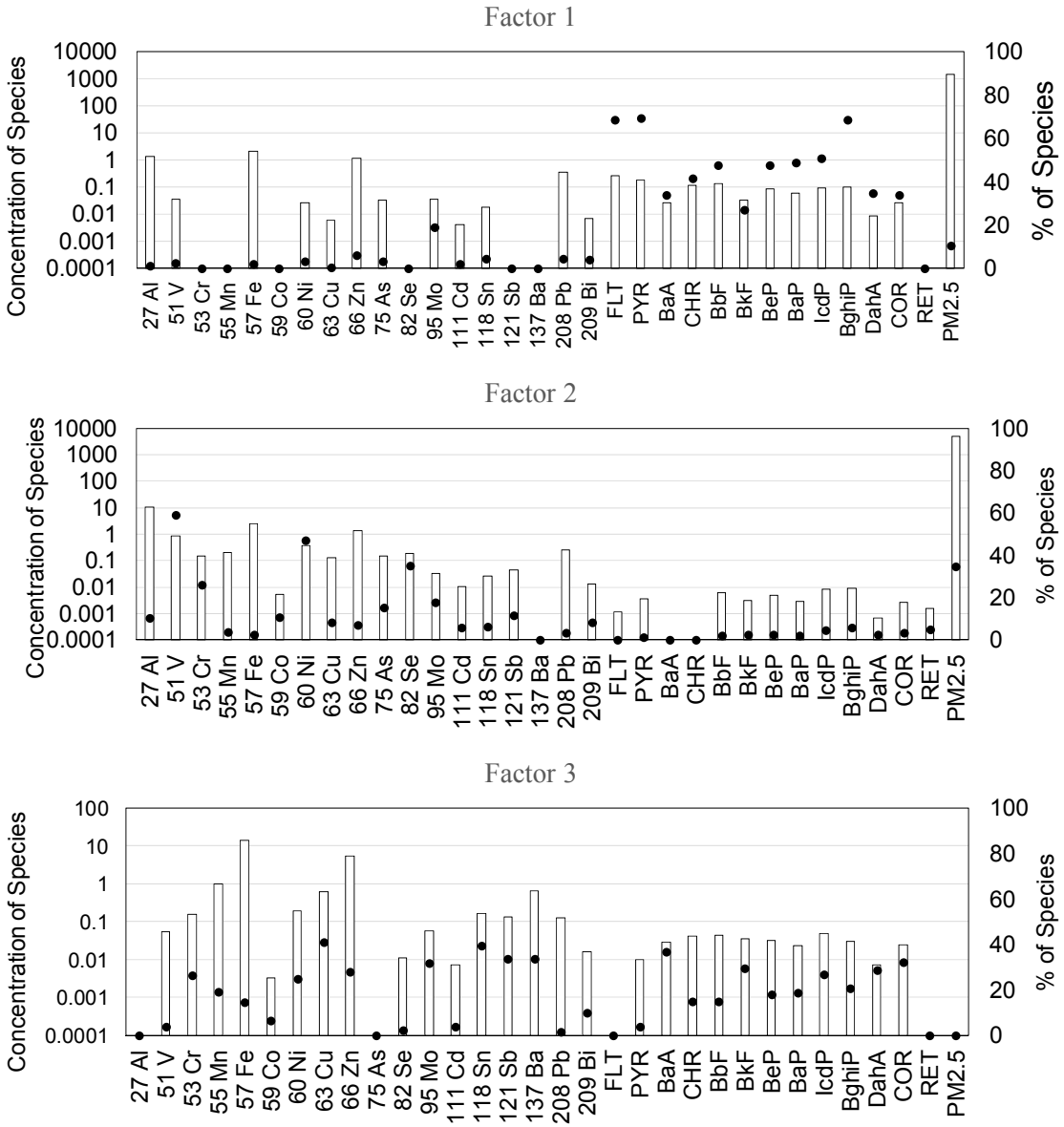


Fig. 7. Factor profiles of the identified six factors.

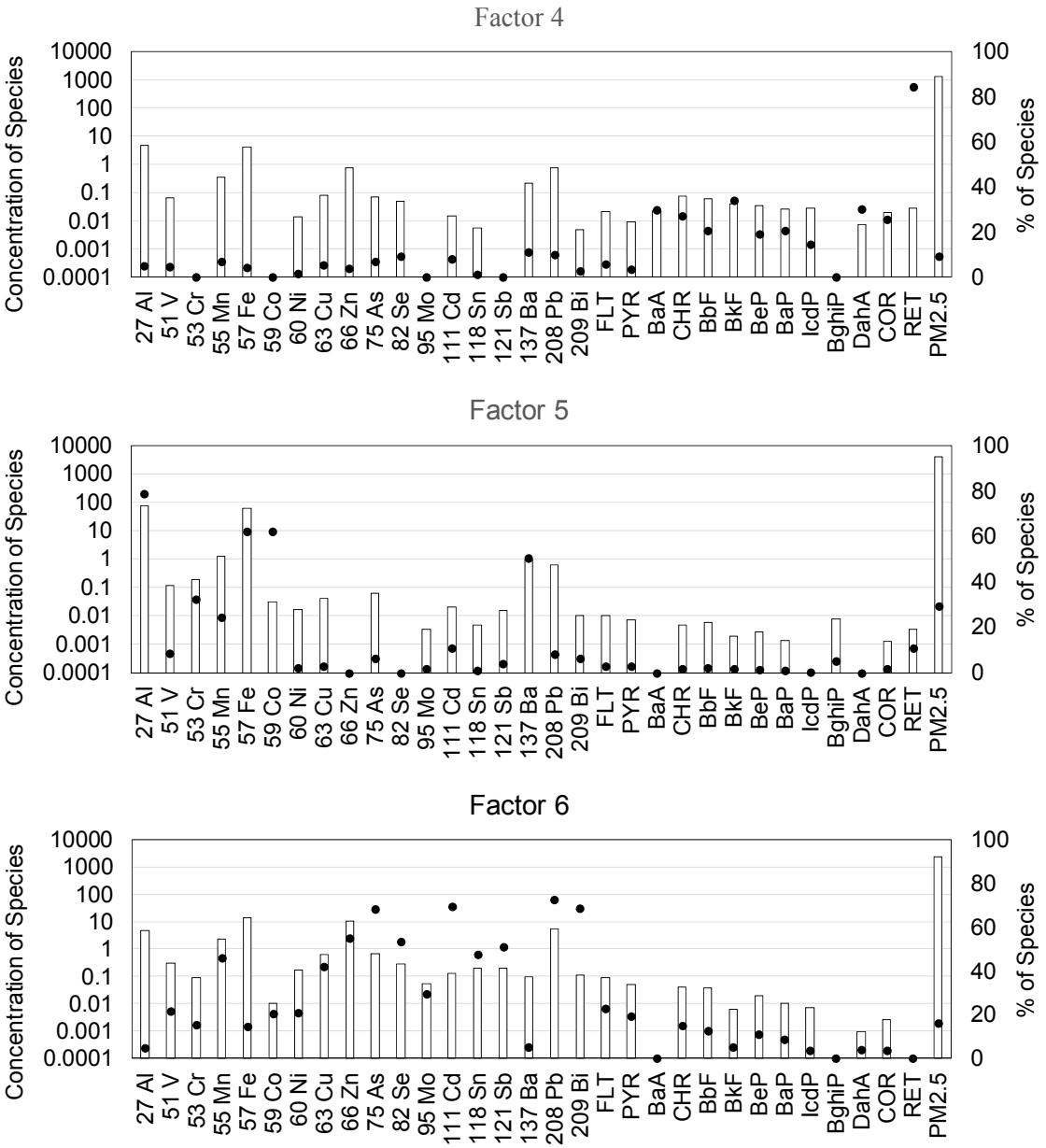


Fig. 7. (*continued*).

(excluding the days when $C_{transboundary} - C_{local\ BB\ and\ SD}$ was less than 0).

Kanaya (2015) ran the regional chemical transport model WRF-CMAQ with emission sensitivity simulations and reported that the contribution of $PM_{2.5}$ from China was 50% and over in Kyusyu area, including Kumamoto. This trend is consistent to ours.

CONCLUSIONS

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous organic components of $PM_{2.5}$ mostly generated by incomplete combustion of organic matters. Since PAHs are known to be carcinogenic and mutagenic, its impact to human becomes a great concern. In Japan, it has been speculated that most PAHs observed in Japan, especially in western Japan be caused by transboundary air pollution (TAP). Thus, it is important to estimate the contribution of TAP to the air quality in Japan must be evaluated.

The event of TAP of PAHs has been reported in numerous studies conducted in Japan. However, no study has attempted to evaluate the quantitative contribution of PAHs from TAP by using a receptor model. In the present study, we developed an index to investigate the contribution of TAP to the air quality in Kumamoto, Japan. Indeno(1, 2, 3-cd)pyrene (IcdP) was selected as the local pollution tracer and Pb was used as the transboundary pollution tracer and it turned out that these tracers varied according to the characteristics of their origins. In addition the positive matrix factorization (PMF) analysis was carried out to identify major sources of the observed PAHs.

The average contribution of TAP on the days when

transboundary pollution is high was evaluated as being 46% based on the IcdP/Pb ratio and PMF. It is the first evaluation of the contribution of TAP caused by PAHs on the basis of measurement data to be conducted in Japan.

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SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at http://www.aaqr.org.

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