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Atmospheric behaviors of polycyclic aromatic hydrocarbons at a Japanese remote

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Abstract

   Total suspended particulates were collected at a Japanese remote background site (Noto Air Monitoring Station; NAMS) on the Noto Peninsula from September 2004 to June 2014. Nine polycyclic aromatic hydrocarbons (PAHs) in the particulates (fluoranthene, pyrene, benz[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, benzo[*ghi*]perylene and indeno[1,2,3-*cd*]pyrene) were determined by HPLC with fluorescence detection. The mean total concentrations of the nine PAHs in the cold season (November to May for the years 2004 – 2014) was 670 pg m^{-3} (range 37 to 4100 pg m^{-3}). The mean total concentration in the warm season (June to October for the same period) was 170 pg m^{-3} (range 31 to 960 pg m^{-3}). The atmospheric PAH level at NAMS decreased in recent years, although no significant change was found in the warm season. An analysis of meteorological conditions showed that the atmospheric PAHs at NAMS were long range transported from Northeast China in the cold seasons and were contributed to by Japanese domestic sources in the warm seasons. Lower concentration ratios of reactive PAHs to their isomers at NAMS also supported these results. Activities associated with the Beijing Olympic and Paralympic Games in 2008 and reconstruction after the 2007 Noto Hanto earthquake may have contributed to the yearly variations of atmospheric PAH levels at NAMS during the period 2007 – 2009. Source control measures implemented by the Chinese and Japanese governments appear to have been effective in decreasing the atmospheric PAH levels at NAMS in recent years.

1. Introduction

Many polycyclic aromatic hydrocarbons (PAHs) have carcinogenic and/or mutagenic (Amens et al., 1975), estrogenic/antiestrogenic (Hayakawa et al., 2007) or antiandrogenic activities (Kizu et al., 2000). PAHs are important organic pollutants in the atmosphere because several of them are considered carcinogenic or probably carcinogenic to humans (IARC, 2012) or contribute to asthma morbidity (Gale et al., 2012). PAHs mainly originate from imperfect combustion of organic matters. The major sources of PAHs in the atmosphere include diesel-engine vehicles (Hayakawa et al., 1995), domestic/city heating (Tang et al., 2005), and industrial processes (Wang et al., 2008) in urban areas and wood combustion (Sienra et al., 2005) and straw combustion (Zhang et al., 2009) in rural areas. In the arctic and other remote sites, atmospheric PAHs are mainly due to the long-range transposition of air masses (Dickhut et al., 2000; Ding et al, 2007; Feng et al., 2007; Halsall et al., 1997; Primbs et al., 2008; Sofowote et al., 2010; Zhu et al., 2014; Wang et al., 2014).

Northeast Asia has become the most industrially active region in the world. As a result, this has led to serious environmental pollution. Our studies in this region over the past 15 years have shown that the main contributors to atmospheric PAHs and NPAHs are automobiles, especially diesel-engine vehicles in Japanese cities (Tokyo, Sapporo, Kanazawa and Toyama) and Seoul, Korea, and coal combustion processes in Shenyang, Fushun and Tieling, China, and Vladivostok, Russia. Atmospheric concentrations of PAHs were 3 - 180 times higher in Chinese and Russian cities than in Japanese and Korean cities (Kakimoto et al., 2000, 2002; Hattori et al, 2007; Tang et al., 2002, 2005), mainly because of the large consumption of coal in China and Eastern Russia (Tang et al., 2005; Chen et al., 2005). Meanwhile, energy consumptions continue to increase in these countries (BP Statistics, 2014).

In our previous studies of PAHs at a Japanese remote background site on the Noto peninsula (Noto Air Monitoring Station: NAMS) from September 2004 to September 2005 (Yang et al., 2007) and their nitrated derivatives from January 2006 to December 2007 (Tang et al., 2014), we found that atmospheric PAHs and NPAHs were strongly influenced by combustion products transported from Northeast China in winter and from Japan in summer. This suggested that this site is useful for estimating variations of atmospheric PAHs and NPAHs in Northeast Asia. In the present study, we re-analyzed our data on atmospheric PAH levels at NAMS from September 2004 to June 2014 to clarify the long-term changes of atmospheric PAH levels, compositions and their possible contributors.

2. Materials and methods

2.1. Sampling

TSP were collected at Kanazawa University Noto Air Monitoring Station (NAMS: Nisifutamata-machi, Wajima City, Ishikawa Prefecture, Japan; 37º23' N, 136º54' E; 60 m above sea level. Our previous reports named this station WAMS (Tang et al., 2014; Yang et al., 2007)), which locates in Noto Peninsula, 2.1 km south from the Japan Sea coast (Fig. 1). No major emission sources of PAHs and other air pollution matter are near the station. TSP were collected by a high volume air sampler (AH-600, Shibata Sci. Tech. Ltd., Saitama, Japan) with a quartz fiber filter (8 inch × 10 inch, 2500QAT-UP, Pallflex Products, Putnam, CT, USA) at a flow rate of 700 L min^{-1} continuously from September 17, 2005 to June 8, 2014. According to previous reports (Tang et al., 2014; Yang et al., 2007), result of preliminary test and other information, the filters were changed newly every week to minimalize secondary reaction of PAHs. After being dried in a desiccator in the dark, the used filters were weighed and then kept in a refrigerator (-20°C) until use. The quartz fiber filters used for collecting particulate-bound PAHs were pre-heated at 600°C for 4 hours

before using it to lower their PAHs blank values. Field blanks, which accompanied samples to the sampling sites, were used to determine any background contamination. Three filters were selected randomly from the same lot number filters. No contamination was found during traveling of blank samples.

2.2. Chemicals

USEPA 610 PAHs mix, a mixture of 16 PAHs including fluoranthene (FR), pyrene (Pyr), benz[*a*]anthracene (BaA), chrysene (Chr), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), BaP, benzo[*ghi*]perylene (BgPe) and indeno[1,2,3-*cd*]pyrene (IDP) were purchased from Supelco Park (Bellefonte, PA, U. S. A). Two internal standards for PAHs (pyrene-d_{10} (Pyr-d_{10}) and benzo[*a*]pyrene-d_{12} (BaP-d_{12})) were purchased from Wako Pure Chemicals (Osaka, Japan). All other chemicals used were of analytical reagent grade.

2.3. Sample treatment and analytical procedures

Sample preparation method was the same as in our previous report (Tang et al., 2005). A piece of each filter containing less than 4 mg of airborne particulates was thoroughly cut into small pieces in a flask. PAHs were extracted ultrasonically twice with benzene/ethanol (3:1, v/v) and then the solution was filtered. Internal standards, Pyr-d_{10} and BaP-d_{12} were added to the flask prior to the ultrasonic extraction. After filtering the organic solution with an HLC-DISK membrane (pore size 0.45 µm, Kanto Chemical Co., Tokyo, Japan), 100 µL of dimethyl sulfoxide (DMSO) was added and then the organic solution was concentrated to 100 µL with rotation evaporator. The DMSO solution was dissolved in 1.0 mL of acetonitrile, and then an aliquot (20 µL) of the solution was injected into the PAH HPLC system.

The nine PAH species were determined by using HPLC with fluorescence detection. The PAH HPLC system consisted of a reversed-phase column (Inertsil ODS-P, 4.6 i.d. x 250 mm, GL Sciences Inc., Tokyo, Japan) with an acetonitrile/water gradient and fluorescence detection. The flow rate was 1 mL min^{-1}. The time program of the fluorescence detector was set to detect at the optimum excitation and emission wavelengths for each PAH. Other conditions were the same as in our previous report (Tang et al., 2005).

2.4. Data analysis

According to our previous reports (Yang et al., 2007; Tang et al., 2014), the air pollution, such as PAHs and NPAHs, at NAMS was strongly influenced by combustion products transport from Northeast China in winter and from Japan in summer. The long-range transport of air masses from the Asian Continent to Japan can be explained by the atmospheric pressure pattern of Northeast Asia in cold seasons (Terada et al., 2002). Because the Siberian High is strong in winter, the Pacific High is strong in summer. SI Fig. SI-1 shows typical back trajectory analysis of air samples collected at NAMS during our sampling periods by using the Meteorological Data Explorer online program (METEX, *http://db.cger.nies.go.jp/metex/*) (Tang et al., 2014). Most of air mass collected at NAMS passed through Northeast China in cold season and passed through Japan in warm season. In this study, in order to clarify the characteristics of PAHs at NAMS in the different pressure pattern, total 455 samples observed at NAMS divide into two groups. One is cold season samples (from November to May of next year: 280 samples) and the other is warm season samples (from June to October: 175 samples). This grouping method was also supported by the data of the Kanazawa Local Meteorological Office, Japan Meteorological Agency (*http://www.jma-net.go.jp/kanazawa/mame/kousa/kousa.html*). As shown in SI Fig. SI-2,

Asian dust events, means the strong Siberian High periods, were always observed in Ishikawa Prefecture from November to May of next year.

3. Results and discussion

3.1. Concentrations

The mean concentrations of the sums of the nine PAHs at NAMS were 670 pg m^{-3} in the cold season, which ranged from 37 to 4100 pg m^{-3} and were 170 pg m^{-3}, in the warm season, which ranged from 31 to 960 pg m^{-3} from 2004 to 2014, respectively. Compared with the PAH concentrations at other remote or rural sites, the concentrations at NAMS were higher than those at Mt. Bachelor Observatory in the United States (Primbs, et al., 2008), but lower than those at Yi Qian and Changdao, China (Feng, et al., 2007; Zhu, et al., 2014).

Figure 2 shows the weekly variations of individual PAH at NAMS from September 17, 2004 to June 8, 2014. The concentrations of all PAHs were elevated in the cold season in every year. The concentrations of PAHs are generally higher in the cold season than in the warm season (Halsall, et a., 1997; Park et al., 2002; Reisen et al., 2005; Tang et al., 2005, 2009). Seasonal variation of atmospheric PAHs is due to changes in sources, weather condition and secondary chemical reactions (Butler and Crossley, 1981; Tang et al., 2005). In the present study, the cold season to warm season (C/W) concentration ratios of PAHs calculated from Fig. 2 ranged from 3.76 to 5.47 for 4-ring PAHs (Pyr, FR, BaA and Chr), ranged from 3.23 to 3.55 for 5-ring PAHs (BbF, BkF and BaP) and ranged from 2.77 to 2.89 for 6-ring PAHs (BgPe and IDP). The C/W concentration ratios of 4-ring PAHs were larger than those of 5- and 6-ring PAHs. This was because that 4-ring PAHs have relatively high vapor pressures and distribute more in the particulate phase at lower ambient temperature (Yamasaki et al., 1982). According to our previous report (Yang et al., 2007), two lines of evidence indicate that atmospheric PAHs at NAMS in the cold season largely come from

Asian continent such as Northeast China: a comparison of the PAH composition of Shenyang in Northeast China to that of Kanazawa which was near NAMS, and an analysis of the meteorological conditions at NAMS.

3.2. Meteorological factors

Table 1 shows the correlation coefficients between each PAH and several meteorological factors. The correlation coefficients were calculated from the weekly averages of each PAH and meteorological data published by the Japan Meteorological Agency (*http://www.jma.go.jp/jma/index.html*). Negative correlations were found between PAH levels and temperature (˚C) in every season. In the warm season, the correlations were strong for 4-ring PAHs ($p < 0.01$, $n = 175$) but weak for 5- and 6-ring PAHs ($p = 0.02 – 0.67$, $n = 175$). Because the vapor pressures of 4-ring PAHs are lower than those of 5- and 6-ring PAHs (Yamasaki et al, 1982), the gas/particle partition of atmospheric 4-ring PAHs increases with increasing temperature (Araki et al., 2009; Bidleman et al., 1986; Sitaras et al., 2004). Therefore, the major sources of atmospheric PAHs at NAMS in the warm season did not appear significantly change. However, the correlations were strong and positive in all PAH levels ($p < 0.01$, $n = 280$) in the cold season. The correlations could not be explained by only the gas/particle partitions which depend on the vapor pressures of the PAHs. The increase in atmospheric PAH levels at NAMS in the cold season seem to be the most convincing cause of the correlations (Tang et al., 2014; Yang et al., 2007). Since strong and negative correlations ($p < 0.01$, $r = -0.4276 - -0.4293$) were observed between temperature and pressure (hPa), the positive correlations between pressure and PAHs ($p < 0.01$ and/or 0.05, except for BbF, BkF and IDP in cold season, $r = 0.089 – 0.3901$) can be explained by similar reasoning, although the correlations between the levels of 5- and 6-ring PAHs and pressure were weak in the cold season. The correlations between sunshine and PAH levels

were negative in the cold season and positive in the warm season, although sunshine (h/w) was strongly and positively correlated with temperature ($p < 0.01$) in every season. The main cause for the high temperature was that the Siberian High (a large cold, dry air mass that accumulates in northeastern Eurasia during the cold season) was weak and the North Pacific High (a subtropical anticyclone in the northeastern Pacific Ocean, that is strongest during the warm season) was strong. Therefore, the concentrations of PAHs transported from Northeast China to NAMS decreased in the cold season, but the concentrations of PAHs transported from other Japanese cites increased (Tang et al., 2014, Yang et al., 2007). In general, atmospheric pollutants including PAHs are negatively correlated with precipitation (mm/w)/humidity (%) (rain and snow) because of a washout effect (Kakimoto et al., 2000). However, no strong negative correlations were found between PAH levels and precipitation/humidity in the cold season. In contrast, most of the PAH levels were strongly and positively correlated with the amount of snowfall (cm w^{-1}) in the cold season, which are the periods of the strong Siberian High. On the other hand, wind speed (m s^{-1}) seemed to have no significant influence on PAH levels in either the warm season or the cold season. These results are in agreement with our previous studies of PAHs and NPAHs (Tamamura et al., 2007; Tang et al., 2014; Yang et al., 2007) and show that the seasonal variations and the major sources of PAHs in the atmosphere at NAMS did not change over the 10-year study period.

3.3. Yearly variations

In the cold season, PAH levels did not significantly change from 2004 to 2006 (Fig. 3-1-L). However, the PAH level was much higher in 2007 than in 2006 ($p = 0.01$), while it was much lower in 2008 than in 2007 ($p < 0.01$), and then the PAH level rose again in 2009 ($p = 0.01$, compared to in 2008). Similar trends were observed in the yearly variations of

TSP levels (Fig. 3-2-L) and PAH in TSP levels (Fig. 3-3-L). PAH in TSP levels was unusually low in 2008. Because the atmospheric PAHs at NAMS were mostly affected by the transport of air pollutants from Northeast China including Beijing in winter (Tang et al., 2014; Yang et al., 2007), changes in the atmospheric PAH level in Northeast China was considered as the likely cause of the yearly variation. In preparation for the Beijing Olympics in August and September of 2008, various measures were implemented to reduce emissions of air pollutants by Beijing and the surrounding regional governments, such as Tianjin, Hebei, Shandong, Shanxi and Inner Mongolia. As a result, air pollutants, such as volatile organic compounds, particulate matters, polychlorinated dibenzo-p-dioxins/dibenzofurans (PCDD/Fs), PAHs and NPAHs were reduced significantly during the games (Li et al., 2011; Liu et al., 2009; Ma et al., 2011; Wang, et al., 2009, 2011; Xin et al., 2010; Zhou et al., 2010). In contrast, higher PAH levels were observed at NAMS in 2007, possibly due to the infrastructure construction in Beijing and other cities before the Olympics. On the other hand, the mean atmospheric PAH level in Beijing in winter was lower in 2008 than in 2006 (Ma et al., 2011; Tao et al., 2007), in agreement with our present study of low PAH levels in 2008. These results suggest that the effects of the source control measures continued for a while. However, some kinds of air pollutants in Beijing, such as TSP and PCDD/Fs, recovered to the high levels in 2009 (Li et al., 2011), possibly because the source control measures were less strictly implemented after the Olympics. A similar trend was observed in the present study. PAH levels in 2009 were significantly higher than those in 2008 ($p = 0.01$) (Fig. 3-1-L). However, the PAH level decreased significantly from 2010 to 2013 ($p = 0.04$). Because the TSP levels in the atmosphere did not show significant change during this period (Fig. 3-2-L), the likely main cause was a decrease of PAH levels in TSP from 2011 to 2013 (Fig. 3-3-L). A similar trend was observed from 2001 to 2007 in Shenyang, which is the largest city in Northeast China and located along the air

transportation route to NAMS (Tang et al., 2007; 2014). Since energy consumption in China has been increasing in recent years (BP Statistics, 2014), the decrease of PAH levels in TSP from 2011 to 2013 indicate that the source control measures implemented by the Chinese government in recent years were working (Li et al., 2011).

In the warm season, atmospheric PAHs at NAMS mainly originated from domestic sources in Japan (Tang et al., 2014; Yang et al., 2007). PAH levels peaked in 2008 (Fig. 3-1-R). TSP levels also increased from 2004 to 2008 ($p = 0.03$) (Fig. 3-2-R), but PAH in TSP level did not change significantly during this period (Fig. 3-3-R). Therefore, we suspect that an increase in one source was causing these yearly variations. It is unclear why the PAH levels increased from 2004 to 2006. However, the high PAH level from 2007 to 2010 might be due to reconstruction after Noto Hanto earthquake (M6.9) on March 25, 2007 (*http://noto-fukkoukikin.jp/index.html*). The PAH level and the PAH in TSP level tended to decrease from 2011 to 2014, although the decreases were not statistically significant ($p = 0.13$ and $p = 0.06$, respectively). Similar yearly variations were observed at a Kanazawa roadside (Hama et al., 2012; Tang et al., 2012). The PAH level decreased by 63% in the winter and by 75.6% in the summer and the NPAH level (total concentrations of 1,3-, 1,6- and 1,8-dinitropyrenes, 1-nitropyrene, 6-nitrochrysene, 7-nitrobenz[*a*]anthracene and 6-nitrobenzo[*a*]pyrene) decreased by 88% in the winter and 89% in the summer from 1999 to 2010, respectively (Hama et al., 2012). The main reason for the decrease of PAH level appeared to be the regulation of exhaust gas/particulates from automobiles. For example, the regulation values of NOx and particulate matter for new diesel vehicle (3500 Kg < GVW) were 5.80 g kWh^{-1} and 0.49 g kWh^{-1}, respectively, up to 2002. These values were subsequently reduced in the following years, reaching 0.7 g kWh^{-1} and 0.010 g kWh^{-1}, respectively (SI Fig. SI-3).

3.4. Compositions

Several PAH diagnostic ratios have been used to indicate the main sources of PAHs in the atmosphere because the compositions of the isomers are strongly associated with the mechanisms of formation of carbonaceous aerosols (Kavouras et al. 2001). The median values of [BaA]/([Chr]+[BaA]) in the cold and warm seasons (0.28 and 0.25, respectively) imply that the sources were coal combustion, traffic and factories (Table 2, Fig. SI-4), in agreement with other studies (Ding et al., 2007; Sienra et al., 2005; Wang et al., 2014; Wang et al., 2008; Zhu et al., 2014; Zhou et al., 2005). The other ratios in both seasons showed the similar trend with the [BaA]/([Chr]+[BaA]) (Table 2, Fig. SI-4). Because no major emission sources of PAHs are near the NAMS and because the air mass collected at NAMS were also occasionally long-range transported from Northeast China in the warm season (Tang et al., 2014; Yang et al., 2007), the atmospheric PAHs at NAMS appear to have originated from various sources.

On the other hand, atmospheric PAHs can undergo photolysis and/or oxidation by reacting with ozone, hydroxyl radical, nitrogen oxide or other strong oxidizing species (Butler and Crossley, 1981). The reactivities of PAHs adsorbed on soot particles were found to be in the order: Anthracene > BaP > BgPe > BaA > Pyr > Benzo[*e*]pyrene > Chr > FR > Phenanthrene ~ Coronene (Butler and Crossley, 1981). The findings of lower [BaA]/([BaA]+[Chr]) and [BeP]/([BeP]+[BaP]]) ratios and/or higher [FR]/([FR]+[Pyr]) and [IDP]/([IDP]+[BgPe]) in rural areas suggested that reactive PAHs are protected from secondary reactions during transport (Feng et al., 2007; Gogou et al., 1996; Hong et al., 2007). The [BaA]/([BaA]+[Chr]) ratio, which is an indicator of the age of an air mass (Cotham and Bidleman, 1995), was lower at NAMS in both seasons than in several city areas (Hong et al., 2007; Sienra et al., 2005; Tang et al., 2005), which suggested that the air mass at NAMS had been in the atmosphere for a long time in both seasons. Moreover, all

diagnostic ratios calculated in this study were significantly lower in the warm season than in the cold season ($p < 0.01$, $n = 175 - 280$), except for the [IDP]/([IDP]+[BgPe]) ratios ($p = 0.34$, $n = 175 - 280$) (Table 2, Fig. SI-4). Because BaA, FR, BbF and BaP are more labile than their isomers during transportation due to their higher reactivities (Butler and Crossley, 1981), these results also suggest that the PAHs at NAMS in the cold season come from more distant sources, in agreement with our previous studies (Tang et al., 2014; Yang et al., 2007).

4. Conclusions

Atmospheric PAH levels at NAMS, which is a remote background site on the Noto peninsula in Japan, were always higher in the cold seasons than in the warm seasons from 2004 to 2014. By analyzing the meteorological conditions (temperature, pressure, sunshine, wind speed, humidity, precipitation and snow), our data show that the main causes of the seasonal variations were changes in the timing of the Siberian High and the Pacific High. In agreement with our previous reports (Tang et al., 2014; Yang et al., 2007), the atmospheric PAHs were long-range transported from Northeast China in the cold seasons and were mainly contributed to by Japanese domestic sources in the warm seasons. These results were supported by the reduced concentrational ratios of reactive PAHs to their isomers at NAMS.

Some events possibly contributed to the yearly variations of atmospheric PAH levels at NAMS from 2004 to 2014. In the cold seasons from 2007 to 2010, the Beijing Olympics appeared to increase PAH levels in 2007 and 2009 and decrease them in 2008. In the warm seasons, reconstruction after the Noto Hanto earthquake appears to be responsible for the higher PAH levels from 2007 to 2010. The source control measures recently implemented by the Chinese and Japanese governments appeared to decrease the atmospheric PAH levels at NAMS in both seasons.

Acknowledgements

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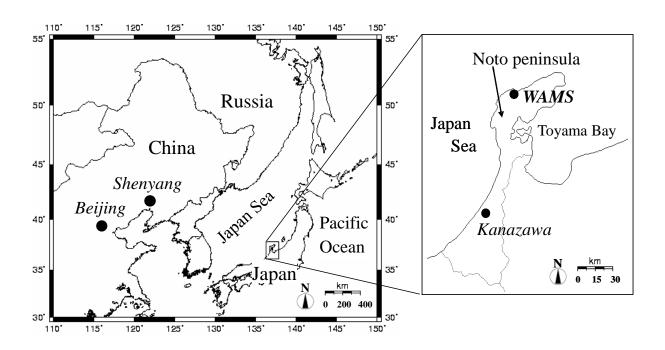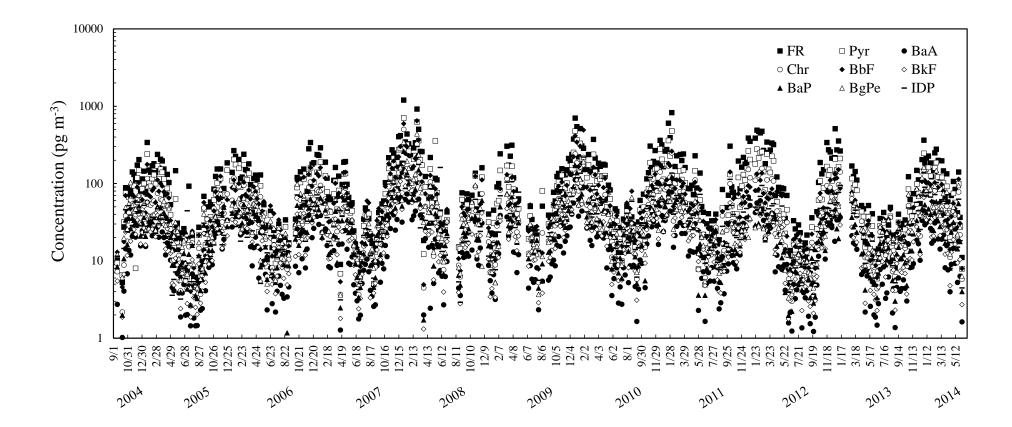
Figure Captions

Fig. 1. Location of sampling site. NAMS: Nisifutamata-machi, Wajima City, Ishikawa Prefecture, Japan; 37º23' N, 136º54' E; 60 m above sea level (Tang et al., 2014).
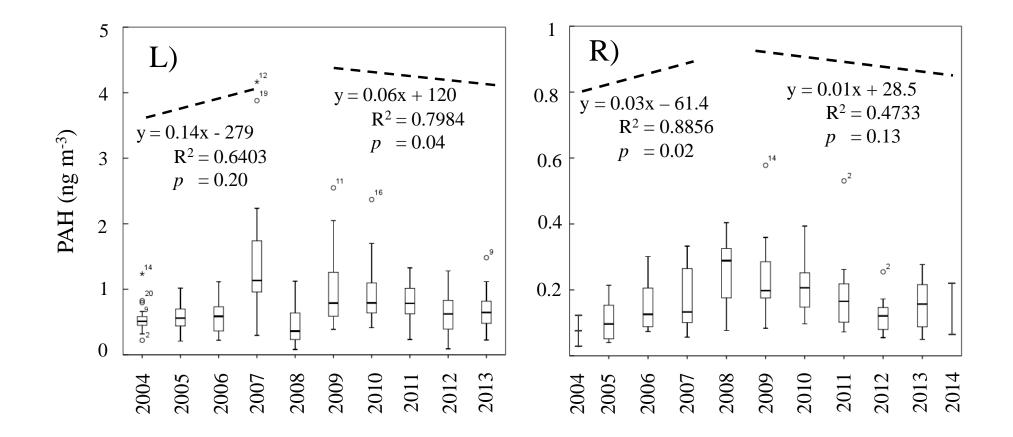
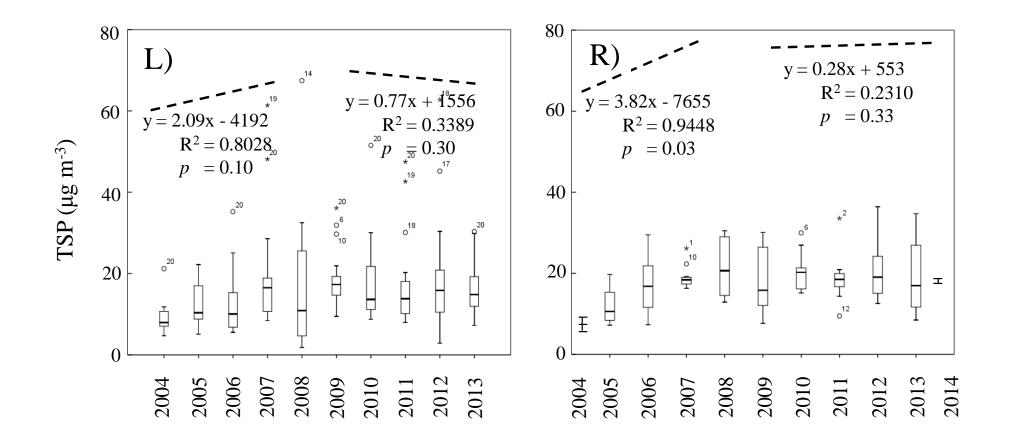**Fig. 2.** Atmospheric PAH levels at NAMS from September 17, 2004 to June 8, 2014.

Fig. 3. Yearly variations of PAHs, TSP, and PAHs in TSP at NAMS in the cold (L) and warm (R) seasons. Upper and lower error bars represent the maximum and the minimum concentrations. The upper and lower edges of the boxes represent the 75th and 25th percentile concentrations. Within each box, median concentrations are shown as solid lines. (A) total levels (ng m^{-3}) of nine PAHs. (B) TSP levels (μg m^{-3}). (C) Total levels of nine PAHs in TSP levels (ng μg^{-1}).
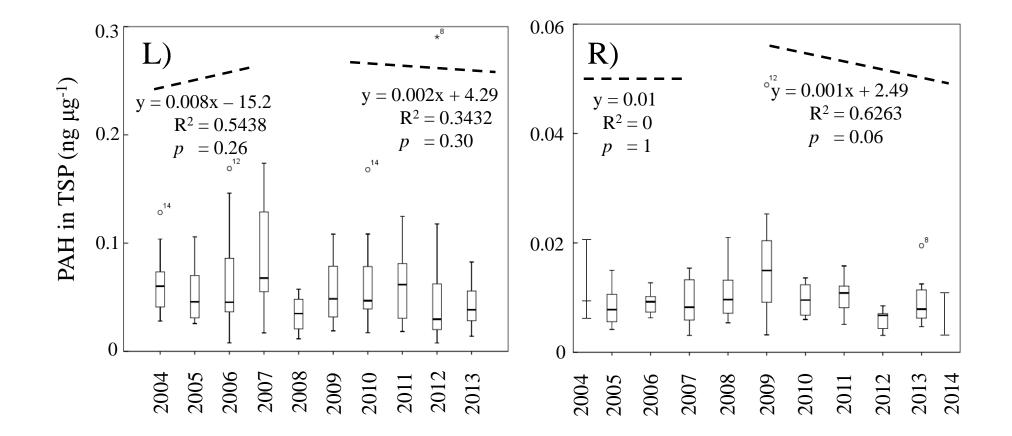
Figure 1

Figure 2

Figure 3(A)

Figure 3(B)

Figure 3(C.)

L)

PAH in TSP (ng μg^{-1})

y = 0.008x − 15.2
R^2 = 0.5438
p = 0.26

y = 0.002x + 4.29
R^2 = 0.3432
p = 0.30

R)

y = 0.01
R^2 = 0
p = 1

y = 0.001x + 2.49
R^2 = 0.6263
p = 0.06

Table 1 Correlation coefficients between nine PAHs and several meteorological factors at NAMS in the cold and warm seasons[a].

	Temperature (°C)		Pressure (hPa)		Sunshine (h w^{-1})		Wind speed (m s^{-1})		Humidity (%)		Precipitation (mm w^{-1})		Snow (cm w^{-1})	
	Cold	Warm	Cold	Warm	Cold	Warm	Cold	Warm	Cold	Warm	Cold	Warm	Cold	Warm
Pressure	-0.4293**	-0.4276**												
Sunshine	0.6519**	0.2768**	-0.2541**	0.1851*										
Wind speed	-0.3508**	-0.0610	-0.0784	0.1725*	-0.2615**	-0.1313								
Humidity	-0.0604	0.0811	0.0615	-0.3950**	-0.4649**	-0.5423**	-0.3301**	-0.365**						
Precipitation	-0.2366**	0.0117	-0.087	-0.1934**	-0.4983**	-0.4953**	0.3146**	0.136	0.3893**	0.4253**				
Snow	-0.5215**	-	0.0792	-	-0.3807**	-	0.2568**	-	0.1838**	-	0.1760**	-		
FR	-0.4524**	-0.3329**	0.2055**	0.3786**	-0.2883**	0.1627*	0.1176*	0.0577	-0.0310	-0.3345**	0.0334	-0.2089**	0.3004**	-
Pyr	-0.4234**	-0.3253**	0.1762**	0.3901**	-0.2492**	0.1909*	0.1237*	0.0339	-0.1004	-0.3899**	0.0044	-0.2246**	0.2769**	-
BaA	-0.4765**	-0.2155**	0.2117**	0.3781**	-0.3687**	0.1872*	0.1622**	0.0423	-0.0104	-0.3657**	0.0709	-0.2364**	0.3638**	-
Chr	-0.3552**	-0.2170**	0.1479*	0.3650**	-0.2379**	0.2339**	0.1038	0.0569	-0.0591	-0.3830**	0.0064	-0.2276**	0.2726**	-
BbF	-0.2895**	-0.1773*	0.1085	0.3293**	-0.2098**	0.2276**	0.0405	0.0426	-0.0401	-0.3554**	-0.0076	-0.1990**	0.2370**	-
BkF	-0.2623**	-0.1496*	0.0893	0.3027**	-0.1794**	0.2213**	0.0496	0.0329	-0.0747	-0.3202**	-0.0337	-0.2007**	0.2220**	-
BaP	-0.2583**	-0.0329	0.1253*	0.2616**	-0.1706**	0.2657**	0.1066	-0.0060	-0.1290*	-0.3581**	-0.0247	-0.2175**	0.1848**	-
BgPe	-0.1892**	-0.1247	0.1305*	0.3456**	-0.1076	0.2200**	-0.027	-0.0057	-0.1411*	-0.3171**	-0.0966	-0.2049**	0.0884	-
IDP	-0.2061**	-0.1936*	0.1132	0.2058**	-0.1234*	0.1605*	-0.005	0.0602	-0.0744	-0.2635**	-0.0506	-0.1640*	0.1711**	-

Level of significance: *: $p < 0.05$; **: $p < 0.01$.

[a]Meteorological data from Japan Meteorological Agency (*http://www.jma.go.jp/jma/index.html*).

Table 2 Diagnostic ratios of atmospheric PAHs from this and previous studies. Median value of each PAH was used in this study.

Source	[BaA]/([Chr]+[BaA])	[FR]/([Pyr]+[FR])	[BbF]/([BbF]+[BkF])	[BaP]/([BaP]+[BgPe])	[IDP]/([BgPe]+[IDP])	Reference
Gasoline-engines	0.22 - 0.55					Simcik et al., 1999
		0.40				Rogge et al., 1993
			0.52 - 0.60			Dickhut et al., 2000
					0.21 - 0.22	Khalili et al., 1995
Factories	0.23 - 0.89	0.21 - 0.26			0.36 - 0.57	Yang et al., 2002
					0.5	Zhang et al., 2008
Diesel-engines	0.38 - 0.64	0.60 - 0.70				Sicre et al., 1987
					0.35 - 0.70	Rogge et al., 1993
	0.36	0.50			0.50	Tang et al., 2005
				0.23 - 0.28		Masclet et al., 1987
Coal stoves	0.50	0.53			0.33	Tang et al., 2005
		> 0.5			> 0.5	Yunker et al., 2002
					0.35 - 0.69	Zhang et al., 2008
				0.47 - 0.86		Daisey et al., 1979
					0.23 - 0.47	Chen et al., 2005
	0.18 - 0.38	0.36 - 0.53	0.81 - 0.95		0.14 - 0.32	Huang et al., 2014
			0.78 - 0.80			Masclet et al., 1987
Cold season	0.28	0.59	0.74	0.44	0.50	This study
Warm Season	0.25	0.56	0.72	0.41	0.48	This study