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Factors affecting atmospheric 1-, 2-nitropyrenes and 2-nitrofluoranthene in winter at Noto peninsula, a  
remote background site, Japan

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## **Abstract**

Airborne particulates were collected at a background site (Wajima Air Monitoring Station; WAMS) on the Noto Peninsula, Japan from January 2006 to December 2007. 1-, 2-nitropyrenes (1-, 2-NPs) and 2-nitrofluoranthene (2-NFR), in the particulates were determined with a sensitive HPLC method with chemiluminescence detection. The average concentrations were higher in winter than in summer. A meteorological analysis indicated that the air samples collected in winter were transported mainly from Northeast China over the Japan Sea. Both the concentration ratios of 2-NFR to 1-NP and 1-NP to pyrene were similar to those in Shenyang in Northeast China which located along the air transportation route to WAMS, but not in Kanazawa which near WAMS. These results strongly suggest that most of the atmospheric 1-, 2-NPs and 2-NFR at WAMS in winter were long range transported from Northeast China.

## **Key words:**

NPAH; PAH; air pollutant; long range transportation; Northeast Asia

## 1. Introduction

Among air pollutants, polycyclic aromatic hydrocarbons (PAHs) and their nitrated derivatives (nitropolycyclic aromatic hydrocarbons, NPAHs) are well-known to be carcinogenic and/or mutagenic (Ames et al., 1975; Epstein et al., 1979; Landvik et al., 2007; Øvrevik et al., 2010; Pedersen et al., 2004, 2005). The International Agency for Research on Cancer has categorized benzo[*a*]pyrene (BaP) and 1-nitropyrene (1-NP) in group 1 (carcinogenic to humans) and 2A (probably carcinogenic to humans), respectively (IARC, 2012, 2013). Atmospheric PAHs and most NPAHs, such as 1-NP, mainly originate from imperfect combustion of organic matter such as petroleum, coal and biomass. For example, urban atmospheric concentrations of 1,3-, 1,6- and 1,8-dinitropyrenes and 1-NP are strongly correlated with traffic volume (Hayakawa et al., 1995), and a 1-NP metabolite in human urine is strongly correlated with exposure to diesel exhaust (Toriba et al., 2007). In addition, some NPAHs such as 2-nitrofluoranthene (2-NFR) and 2-nitropyrene (2-NP) are formed in the atmosphere. Hydroxyl radical-initiated reactions contribute to the formation of 2-NFR and 2-NP while nitrate radical-initiated reactions contribute to the formation of 2-NFR only in nighttime (Arey et al., 1986, 1989; Sweetman et al., 1986). Therefore, PAHs and NPAHs need to be monitored because of their health risks to humans.

Today, Northeast Asia is the most industrially active region in the world. However, this has led to serious environmental pollution. Our studies in this region over the past 15 years have shown that the main contributors to the atmospheric PAHs and NPAHs were 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). Furthermore, PAHs as well as acid rain and Asian Dust (Yellow Sand) were long-range transported from the Asian continent to Japan during the winter heating period of North China (Tamamura et al., 2007; Yang et al., 2007). 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 NPAHs are highly-reactive (Fan et al., 1996; Feilberg and Nielsen, 2000; Kameda et al., 2011; Liu et al., 2012; Miet et al., 2009a, b and c; Ringuet et al., 2012b; Zhang et al., 2011), and because several of their derivatives, such as hydroxylated NPAHs, are considered toxic (Kameda et al., 2008), monitoring atmospheric NPAHs is important to clarify how they transported from Northeast Asia to other areas. In order to predict movements of atmospheric particulates from Northeast Asia, it is helpful to

monitor background sites such as the Noto Peninsula, Japan (Tsapakis and Stephanou, 2007; Yang et al., 2007). In the past, we did not monitor atmospheric NPAHs on the Noto Peninsula because their concentrations were too low to be detected by our conventional HPLC-chemiluminescence detection (CLD) system (Hayakawa et al., 2001; Murahashi and Hayakawa, 1997; Tang et al., 2003). Recently, we developed a more sensitive system for measuring trace levels of NPAHs by modifying the conventional system (Hayakawa et al., 2011).

In the present study, we used this system to analyze total suspended particulates (TSP) on the Noto Peninsula over an approximately two-year period. We determined the concentrations of 1-NP, which is a typical NPAH that is mainly produced by combustion systems, especially diesel-engine vehicles, and 2-NP and 2-NFR, which are typical NPAHs formed in the atmosphere. We also determined the concentrations of PAHs in the same samples to better understand the seasonal variations of NPAHs and their major sources in winter.

## **2. Materials and Methods**

### *2.1. Sampling*

TSP were collected at Kanazawa University Wajima Air Monitoring Station (WAMS: Nisifutamata-machi, Wajima City, Ishikawa Prefecture, Japan; 37°23' N, 136°54'; 60 m above sea level), which locates in Noto Peninsula, 2.1 km south from the Japan Sea coast (Fig. 1). This station is the former National Wajima Acid Rain Monitoring Station of the Ministry of the Environmental Agency, Japan. No major emission sources of PAHs and NPAHs 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 continuously from January 13, 2006 to December 28, 2007. According to previous reports (Yang et al., 2007), result of preliminary test and other information, the filters were changed newly every week to minimize secondary formation of NPAHs. The description of the sampling design is presented in Supplementary Material Section 1. 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 and NPAHs were pre-heated at 600°C for 4 hours before using it to lower their PAHs and NPAHs 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*

1-NP and 2-NFR were purchased from Aldrich Company Inc. (Milwaukee, WI, USA). 2-NP was kindly supplied by Professor Akihisa Hirayama, Kyoto Pharmaceutical University. Deuterated 1-NP (1-NP-*d*<sub>9</sub>), internal standard for NPAHs, was purchased from CDN Isotopes Inc. (Pointe-Claire, Quebec, Canada). All other chemicals used were of analytical reagent grade.

### 2.3. Sample preparation

Sample preparation method was the same as in our previous report (Hayakawa et al., 2011). In order to remove interfering matter originated from the filter, only one-fourth of the filter was used to extract NPAHs. The filter was cut into small pieces in a flask and 100  $\mu$ L of 1-NP-*d*<sub>9</sub> standard solution was added to the flask as an internal standard. Then, NPAHs were extracted ultrasonically twice with benzene/ethanol (3:1, v/v). The solution was washed successively with sodium hydroxide solution, sulfuric acid solution and water. After filtering the organic solution with an HLC-DISK membrane (pore size 0.45  $\mu$ m, Kanto Chemical Co., Tokyo, Japan), the solution was evaporated to dryness. The residue was dissolved in 1.0 mL of ethanol, and then an aliquot (100  $\mu$ L) of the solution was injected into the HPLC-CLD system.

### 2.4. Analytical method

According to our previous report (Hayakawa et al., 2011), the system consisted of four HPLC mobile phase pumps and a chemiluminescence reagent solution pump (LC-10A, Shimadzu, Kyoto, Japan), a chemiluminescence detector (CLD-10A, Shimadzu), a system controller (SCL-10A, Shimadzu), an integrator (Chromatopac C-R7A plus, Shimadzu), a degasser (DGU-14A, Shimadzu), two column ovens (CTO-10AC, Shimadzu) for the reducer column (80°C) and for the clean-up and separator columns (20°C), an auto sample injector (SIL-10A, Shimadzu), a switching valve (FCV-14AH, Shimadzu), a guard column (Spheri-5 RP-18, 4.6 i.d.  $\times$  30 mm, PerkinElmer, Waltham, MA, USA) for clean-up column, a guard column (Shodex Asahipak ODA-50G 6A, 6.0 i.d.  $\times$  10 mm, Showa Denko, Tokyo, Japan) for concentrator column, a concentrator column (Spheri-5 RP-18, 4.6 i.d.  $\times$  30 mm, PerkinElmer), a clean-up column (Cosmosil 5C18-MS-II, 4.6 i.d.  $\times$  150 mm, Nacalai Tesque, Kyoto, Japan), a reducer column (4.0 i.d.  $\times$  10 mm, packed with Pt/Rh, Shimadzu) and two separator columns (Cosmosil 5C18-MS-II, 4.6 i.d.  $\times$  150 mm, Nacalai Tesque and 5C18-AR-II, 4.6 i.d.  $\times$  250 mm, Nacalai Tesque) connected in series.

The mobile phase for the clean-up column and reducer column was a mixture of ethanol and 20 mM acetate buffer (pH 5.5) (3:1, v/v) at a flow rate of 0.3 ml/min. The mobile phase for the concentrator column was the same

ethanol-acetate buffer with 30 mM ascorbic acid at a flow rate of 1.8 ml/min. The mobile phase for the separator columns was a mixture of acetonitrile and 10 mM imidazole buffer (pH 7.6) (1:1, v/v) at a flow rate of 1.0 ml/min. The chemiluminescence reagent solutions were acetonitrile solutions containing 0.4 mM bis(2,4,6-trichlorophenyl)oxalate (TCPO) and 30 mM hydrogen peroxide, respectively, each cooled with ice-water. Both solutions were mixed (1:1, v/v) in the system, and the flow rate of the mixture was 1.0 ml/min. Other conditions were the same as in our reports (Hayakawa et al., 2001, 2011; Tang et al., 2003).

Under the above conditions, the detection limits ( $S/N = 3$ ) of 2-NFR, 2-NP and 1-NP were 4 (2.8), 10 (7.0) and 1 (0.7) fmol/100  $\mu\text{l}$  ( $\text{fg}/\text{m}^3$ ), respectively. These values were better than the values obtained by the previous system. For example, the previous detection limit of 1-NP was 10 fmol (Tang et al., 2005). The calibration curves were straight in the ranges from 10 fmol to 10 pmol (2-NFR), from 50 fmol to 50 pmol (2-NP) and from 5 fmol to 10 pmol (1-NP), respectively, with correlation coefficients over 0.999 and RSDs less than 5% (Hayakawa et al., 2011).

### 2.5. Back trajectory analysis

Three days back trajectory was calculated for every day during the sampling period. The source of the air samples was predicted with the online program, Meteorological Data Explorer (METEX, <http://db.cger.nies.go.jp/metex/>), which was developed by the National Institute for Environmental Studies, Japan. Meteorological data was obtained from the European Centre for Medium-range Weather Forecasting. The system calculates three-dimensional air mass trajectories (height, longitude and latitude) with a time resolution of 6 h and horizontal resolution  $2.5^\circ \times 2.5^\circ$  and vertical resolution was 15 equal levels from surface pressure to 10 hPa (Yang et al., 2007).

## 3. Results and Discussion

### 3.1. Monthly variations

Atmospheric NPAHs originate from imperfect combustion of organic matter, such as 1-NP, and are usually higher in winter than in summer in several cities in East Asia (Kakimoto et al., 2000, 2002; Hattori et al, 2007; Tang et al., 2002, 2005). Possible causes for the seasonal variation include enhanced emissions from residential and/or commercial heating and the formation of a temperature inversion in the boundary layer in winter, and photochemical degradation of NPAHs in summer (Fan et al., 1996; Fujitani, 1986; tang et al., 2005). However, in some parts of Japan and the United States, the concentrations of 2-NFR and/or 2-NP are lower in winter than in warmer seasons (Bamford

and Baker, 2003; Kameda et al, 2004; Murahashi et al., 1999; Reisen and Arey, 2005). In the present study, the concentrations of 1-, 2-NPs and 2-NFR were elevated in the winter seasons (Jan. - Apr. 2006, Oct. 2006 - May 2007 and Oct. - Dec. 2007) (Fig. 2, Supplementary Material Section 2). The three peaks were well synchronized ( $r = 0.4109 - 0.7461$ ,  $p < 0.01$ ,  $n = 99$ ). We previously found that most atmospheric PAHs at WAMS and at a rural site in Kanazawa came from Northern China during the heating period, which generally lasts from late October to beginning April (Tamamura et al., 2007; Yang et al., 2007). The periods of high NPAH levels at WAMS (Fig. 2) approximately coincided with the heating period in Northern China. Furthermore, 1-NP, which, like PAHs, is mainly formed through combustion of fossil fuels, and 2-NP and 2-NFR were strongly correlated with PAHs concentrations at WAMS (Table 1). The concentrations of atmospheric PAHs and NPAHs were much higher in the heating period of Northeast Asia such as Shenyang, Fushun and Tieling, China and Vladivostok, Russia (Hattori et al., 2007; Tang et al., 2002; 2005). These above results suggest that the high NPAH levels detected at WAMS possibly largely come from Northeast Asia, in agreement with our previous studies of PAHs (Tamamura et al., 2007; Yang et al., 2007).

In each year, the mean concentrations of the three NPAHs were in the decreasing order: 2-NFR > 1-NP > 2-NP, in agreement with other studies for similar typology of sampling site (Albinet et al., 2007b, 2008; Bamford and Baker, 2003; Feiberg et al., 2001; Murahashi and Hayakawa, 1997; Reisen and Arey, 2005; Ringuet et al., 2012c; Zimmermann et al., 2012). The mean concentrations of the three NPAHs at WAMS were much lower than those in other rural and background areas (Bamford and Baker, 2003; Feiberg et al., 2001; Reisen and Arey, 2005), which suggests that WAMS is a suitable background site for monitoring atmospheric NPAHs influenced by other areas in East Asia. The concentrations of all NPAHs in 2007 were lower than those in 2006, but the difference of each NPAH was not statistically significant ( $p > 0.07$ ,  $n = 45 - 50$ ).

### 3.2. Meteorological factors

Table 2 shows the correlation coefficients between each NPAH and several meteorological factors. The correlation coefficients were calculated from the monthly averages of each NPAH and meteorological data published by the Japan Meteorological Agency (<http://www.jma.go.jp/jma/index.html>). 2-NFR and 1-NP levels were strongly and positively correlated with the number of snowy days (d/M) and were strongly and negatively correlated with temperature (°C) and the number of sunshine hours per month (h/M). The similar relationships were observed between 2-NP and these meteorological factors, although the correlations were not statistically significant, except for temperature ( $p < 0.01$ ,  $n = 24$ ). Furthermore, no correlations were found between any of the NPAHs and precipitation



(mm/M). However, since 2-NP and 2-NFR are known to be formed secondarily in the atmosphere via photochemical reactions (Arey et al., 1986; 1989; Sweetman et al., 1986), higher atmospheric concentrations of 2-NP and 2-NFR were expected in summer which has higher temperatures and more hours of sunshine (Bamford and Baker, 2003; Kameda et al., 2004; Murahashi et al., 1999; Reisen and Arey, 2005). In addition, atmospheric pollutants including NPAHs are known to be negatively correlated with precipitation (rain and snow) because of a washout effect (Kakimoto et al., 2000). Therefore, the difference between the WAMS data and the above reference data means that most of the atmospheric NPAHs at WAMS in winter did not form locally.

Back trajectory analysis (BTA) is a tool for determining the transport of air masses. It has also been used to find the transport route of air pollutants including PAHs (Liu et al., 2007; tamamura et al., 2007; Yang et al., 2007). We estimated the origins of air masses to WAMS for each day of the sampling period (from 13 January 2006 to 28 December 2007) using BTA as described previously (Yang et al., 2007). For parameters, we used 72 h before present as the time of interest and 1500 m above ground level as the altitude of interest because air transport from Northeast Asia to WAMS usually takes less than 2 days and passes through the free troposphere layer (1 - 2 km above the ground). For air mass collected at WAMS, about 90% of the back trajectories in winter (Fig. 3A, C, D, F), when NPAH levels were high, and about 20% in summer (Fig. 3B, E), when NPAH levels were low, passed through Northeast China. These results also mean that most of the atmospheric NPAHs collected at WAMS during the heating period were long range transported from Northeast China, as was the case for PAHs (tamamura et al., 2007; Yang et al., 2007).

Asian Dust originates in the desert and loess area in the inner Asian continent and is transported over the Pacific region (Husar et al., 2001; Uno et al., 2001). It can accumulate anthropogenic nitrate, sulfate and PAHs on their surfaces by adsorption during transport (Fang et al., 2005; Iwasaka et al., 1988). During the sampling period, the Japan Meteorological Agency detected eight Asian Dust events at WAMS (March 21, April 8, 18, 24 and 25 in 2006 and April 2, May 25 and 27 in 2007). In previous sampling at WAMS (September 17 2004 to September 16 2005), we found that Asian Dust increased TSP but not always PAHs (Yang et al., 2007). However, as shown in Fig. 2, the concentrations of NPAHs of May 2007 were higher than those of May 2006. Total concentrations of PAHs ( $490 \text{ pg/m}^3$ ) of May 2007 were also higher than those of May 2006 ( $300 \text{ pmg/m}^3$ ). In general, there is little long range transport of air pollutants in May because the Siberian High is comparatively weak in this period. In fact, from 2005 (Yang et al., 2007) to 2007, the only Asian Dust events to occur in May at WAMS occurred in 2007 (May 25 and 27). These results also support the idea that the high NPAH levels observed at WAMS were caused by long range transport

from Northeast China. Some of the NPAHs transported from Chinese continent might have been carried by Asian Dust event (Tamamura et al., 2007; Fang et al., 2005), as was found to be the case for other air pollutants (Iwasaka et al., 1988).

### 3.3. Compositions

2-NP and 2-NFR are formed in the atmosphere mainly by the hydroxyl radical and nitrate radical pathways, with [2-NFR]/[2-NP] concentration ratios of about 10 and 100, respectively (Arey et al., 1986, 1989, 1990; Ciccioli et al., 1996; Feiberg et al., 2001; Sweetman et al., 1986; Tsapakis and Stephanou, 2007). At WAMS, the average [2-NFR]/[2-NP] ratios were ranged from 8.61 (Oct. - Dec., 2007) to 13.2 (Jan. - Apr., 2007) (Fig. 4 A), which mean that atmospheric 2-NP and 2-NFR at WAMS were mainly formed by the hydroxyl radical pathway, in agreement with previous studies (Bamford and Baker, 2003; Ciccioli et al., 1996; Feiberg et al., 2001; Hien et al., 2007; Miller-Schulze et al., 2010; Murahashi and Hayakawa, 1997; Murahashi et al., 1999; Reisen and Arey, 2005).

An atmospheric 2-NFR to 1-NP concentration ratio of about 5 or more indicates that NPAHs are mainly formed in the atmosphere (Ciccioli et al., 1996). At WAMS, the average [2-NFR]/[1-NP] ratios were ranged from 2.83 (Jan. - Apr., 2006) to 4.80 (May - Sep., 2007) (Fig. 4 B), which suggest the NPAHs at WAMS were mainly produced by combustion processes. However, in fact, there are no major emission sources such as factories of main roads near WAMS. By comparing the median winter [2-NFR]/[1-NP] ratio at WAMS with that at downtown Shenyang, which is located on the air transportation route to WAMS, and on a main road in Kanazawa, 80 km south of WAMS, the value at WAMS (2.3,  $n = 22$ ) was very close to the value at downtown Shenyang (2.2,  $n = 5$ : TSP were collected from Jan. 26 to Feb. 10, 2010, data are not published) and was significantly larger than that on the main road in Kanazawa (0.9,  $n = 8$ ,  $p < 0.01$ : TSP were collected from Jan. 21 to 29, 2008, data are not published). Furthermore, according to our previous studies (Hattori et al., 2007; Tang et al., 2005), the main contributors of NPAHs, except for 2-NP and 2-NFR, and PAHs in winter were motor vehicles in Japanese commercial cities such as Tokyo, Sapporo and Kanazawa, while they were coal heating systems and factories in the cities of Northeast China such as Shenyang, Fushun and Tieling. We also reported that the [1-NP]/[Pyr] ratio is an useful indicator to estimate the contribution of automobiles and coal combustion systems (Tang et al., 2005). At WAMS, the median winter [1-NP]/[Pyr] ratio (for the periods January - March 2006 and January - March 2007) was 0.007 (range 0.005 to 0.010), which was much smaller than the winter ratios in Kanazawa (0.13), Sapporo (0.14) and Tokyo (0.13) (Tang et al., 2005), but not significantly different from the winter ratios in Shenyang (0.003), Fushun (0.003) and Tieling (0.003) (Hattori et al., 2007). These findings indicate

that the NPAHs detected at WAMS were long range transported from Northeast China. Since 1-, 2-NPs and 2-NFR absorbed to combustion particulates are decomposed by solar radiation and their half-lives under the same conditions are similar (Fan et al., 1996), large amounts of 1-, 2-NPs and 2-NFR were produced in Northeast China including Shenyang (1-NP:  $220 \pm 150 \text{ pg/m}^3$ ; 2-NP:  $260 \pm 180 \text{ pm/m}^3$ ; 2-NFR:  $410 \pm 280 \text{ pg/m}^3$ , on Jan. 26 to Feb. 10, 2010) and then transported to WAMS in winter with the similar composition.

#### **4. Conclusion**

In conclusion, by comparing the concentrations, monthly variations and composition of atmospheric NPAHs and by analyzing the meteorological conditions at WAMS from 2006 to 2007, we showed that the atmospheric NPAHs at WAMS were mostly affected by the transport of air pollutants from Northeast China in winter. This is the first report to describe the long-range transport of NPAHs in East Asia. Most studies have assumed that the amounts of 2-NP and 2-NFR as a percentage of total atmospheric NPAHs increases with time because they can be formed via various radicals and because other NPAHs are photodecomposed (Bamford and Baker, 2003; Kameda et al., 2004). However, in our research, no significant changes of their composition were observed during their transport about 2 days (Fig. 3). This may be because the concentrations of reactive species, such as Pyr, FR, are diluted too much as they cross the Japan Sea (East Sea) to significantly participate in secondary reactions.

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**Table 1**

Correlation coefficients among selected NPAHs and PAHs.

Compound	2-NFR	2-NP	1-NP	FR	Pyr	BaA	Chr	BbF	BkF	BaP	BgPe
2-NP	<b>0.4109</b>										
1-NP	<b>0.7461</b>	<b>0.3204</b>									
FR	<b>0.8483</b>	<b>0.3773</b>	<b>0.8058</b>								
Pyr	<b>0.8611</b>	<b>0.3969</b>	<b>0.8307</b>	<b>0.9764</b>							
BaA	<b>0.8615</b>	<b>0.3796</b>	<b>0.8299</b>	<b>0.9744</b>	<b>0.9823</b>						
Chr	<b>0.8770</b>	<b>0.3919</b>	<b>0.8197</b>	<b>0.9763</b>	<b>0.9866</b>	<b>0.9839</b>					
BbF	<b>0.8808</b>	<b>0.4194</b>	<b>0.7506</b>	<b>0.9209</b>	<b>0.9213</b>	<b>0.9031</b>	<b>0.9188</b>				
BkF	<b>0.8368</b>	<b>0.3908</b>	<b>0.6875</b>	<b>0.8374</b>	<b>0.8480</b>	<b>0.8185</b>	<b>0.8635</b>	<b>0.9070</b>			
BaP	<b>0.8867</b>	<b>0.4356</b>	<b>0.7690</b>	<b>0.9023</b>	<b>0.9215</b>	<b>0.9027</b>	<b>0.9237</b>	<b>0.9836</b>	<b>0.9213</b>		
BgPe	<b>0.8730</b>	<b>0.4279</b>	<b>0.7448</b>	<b>0.8594</b>	<b>0.8899</b>	<b>0.8700</b>	<b>0.9000</b>	<b>0.9561</b>	<b>0.9016</b>	<b>0.9762</b>	
IDP	<b>0.8383</b>	<b>0.4158</b>	<b>0.6806</b>	<b>0.8774</b>	<b>0.8656</b>	<b>0.8473</b>	<b>0.8689</b>	<b>0.9797</b>	<b>0.8855</b>	<b>0.9600</b>	<b>0.9462</b>

Level of significance:  $p < 0.01$  ( $n = 89 - 99$ ).

Symbols: FR: fluoranthene; Pyr: pyrene; BaA: benz[*a*]anthracene; Chr: chrysene; BbF: benzo[*b*]fluoranthene; BkF: benzo[*k*]fluoranthene; BaP: benzo[*a*]pyrene; BgPe: benzo[*ghi*]perylene; IDP: indeno[1,2,3-*cd*]pyrene.

The determination method of PAHs in the same samples was the same as our previous report (Yang et al., 2007).

Samples ( $n = 10$ ) whose concentrations of 2-NP were lower than the determination limit were omitted for the calculation.

**Table 2**Correlation coefficients between three NPAHs and several meteorological factors at WAMS<sup>a</sup>.

Compound	Snow (d/M)	Precipitation (mm/M)	Temperature (°C)	Sunshine (h/M)
2-NFR	<b>0.4869*</b>	0.1038	<b>-0.7590**</b>	<b>-0.6744**</b>
2-NP	0.3234	0.0675	<b>-0.5247**</b>	-0.3894
1-NP	<b>0.7626**</b>	0.0710	<b>-0.8653**</b>	<b>-0.7228**</b>

Level of significance: \*:  $p < 0.05$ ; \*\*:  $p < 0.01$  ( $n = 24$ ).<sup>a</sup>Meteorological data from Japan Meteorological Agency (<http://www.jma.go.jp/jma/index.html>).

## Figure Captions

**Fig. 1.** Location of sampling site. WAMS: Nisifutamata-machi, Wajima City, Ishikawa Prefecture, Japan; 37°23' N, 136°54' E; 60 m above sea level.

**Fig. 2.** Monthly variations of 1- , 2-NPs and 2-NFR at WAMS during the sampling period. The symbols indicate median concentrations of each NPAH. Error bars indicate the range from minimum to maximum concentrations of each NPAH.

**Fig. 3.** Back trajectory analysis of air samples collected WAMS by using METEX in the six indicated periods. A): January - April, 2006; B): May - September, 2006; C): October - December, 2006; D): January - April, 2007; E): May - September, 2007; F): October - December, 2007. METEX online program: <http://db.cger.nies.go.jp/metex/>.

**Fig. 4.** Atmospheric [2-NFR]/[2-NP] (A) and [2-NFR]/[1-NP] (B) ratios in the six indicated periods same as in Fig. 3. Each column and vertical bar represent mean value and S.D.

Fig. 1.

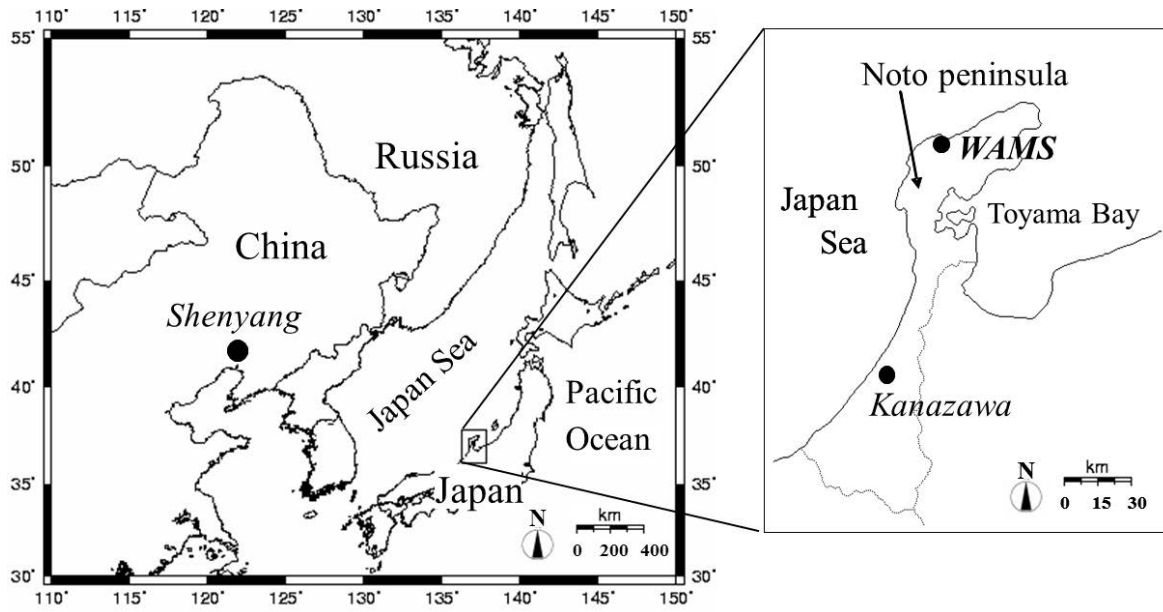
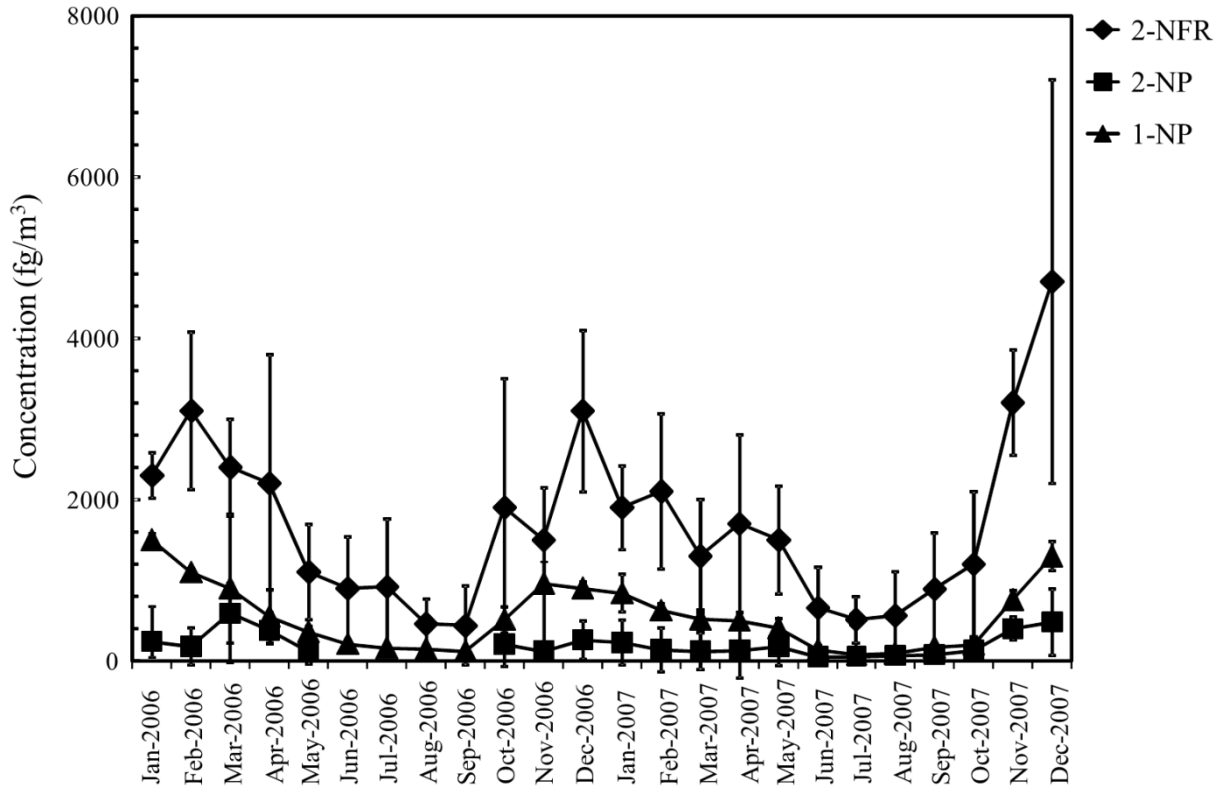
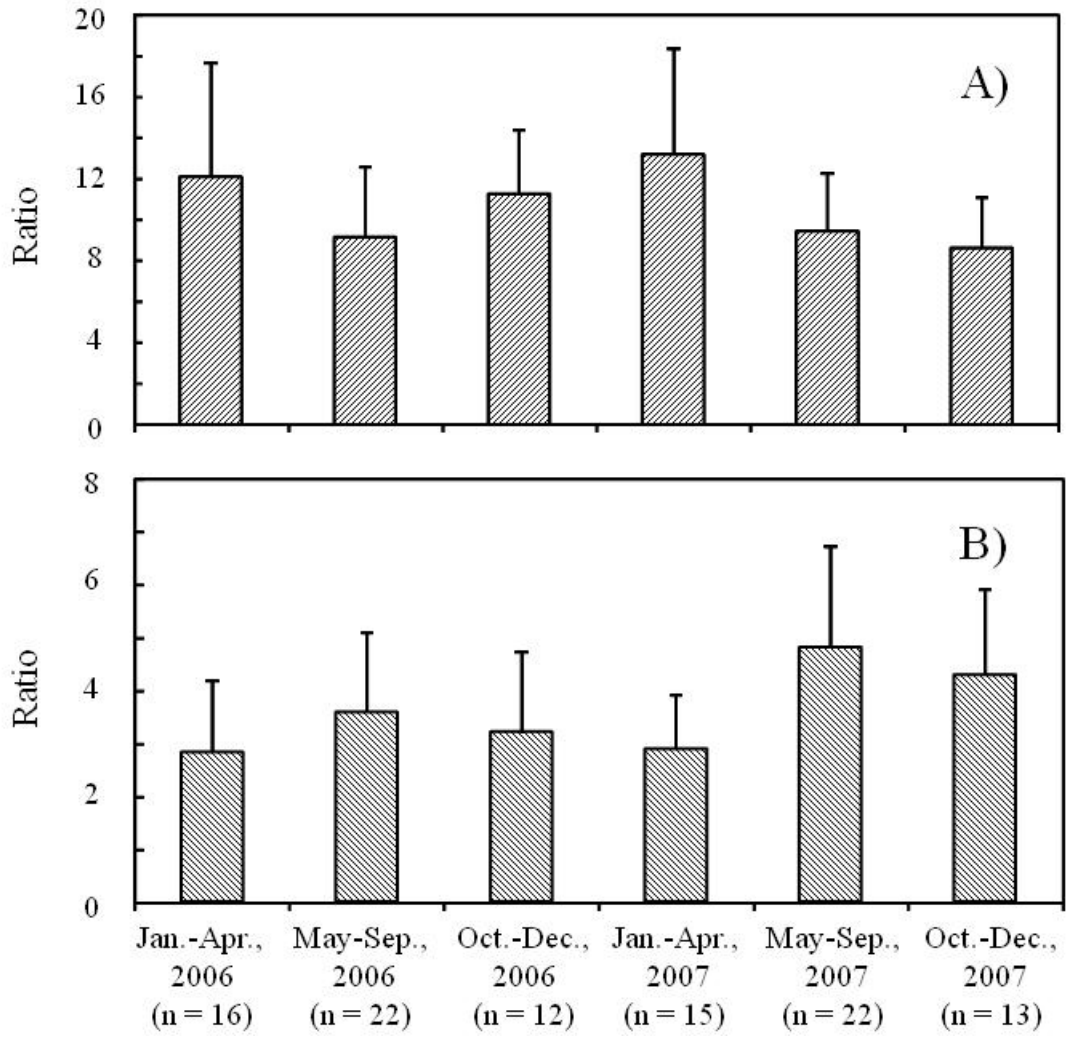


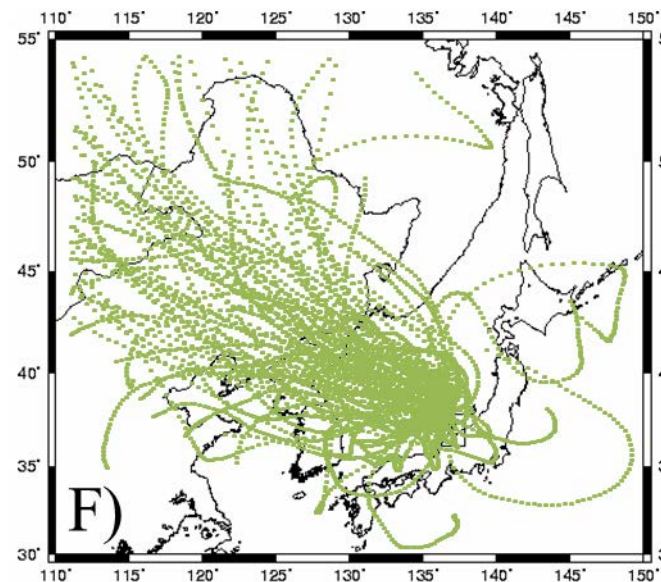
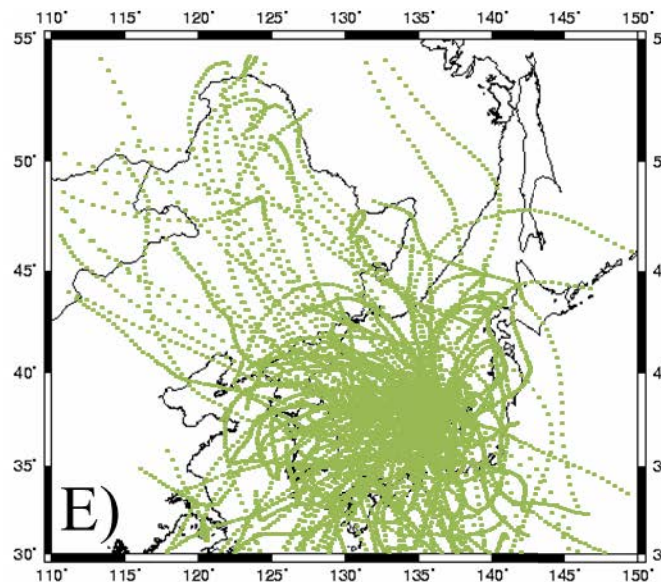
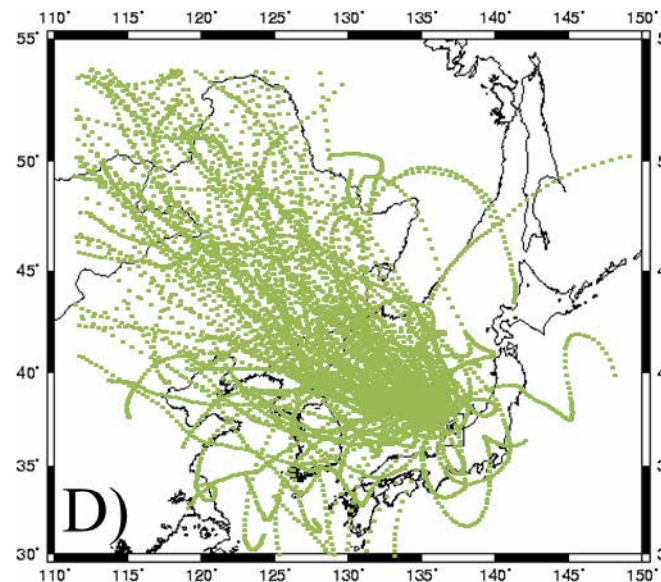
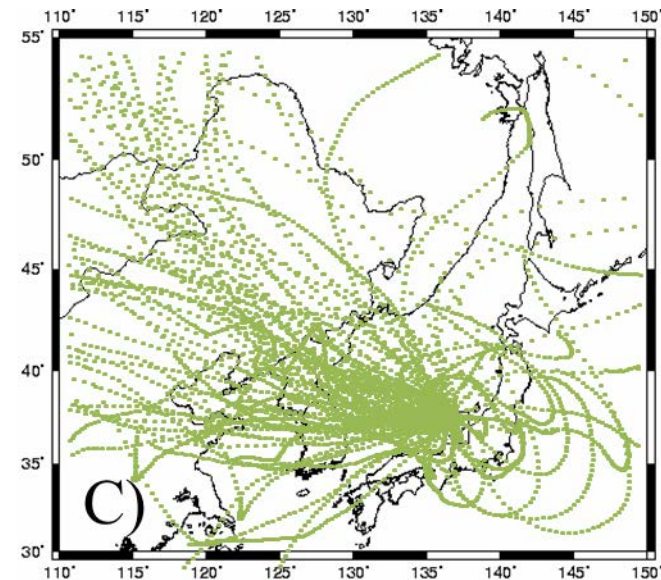
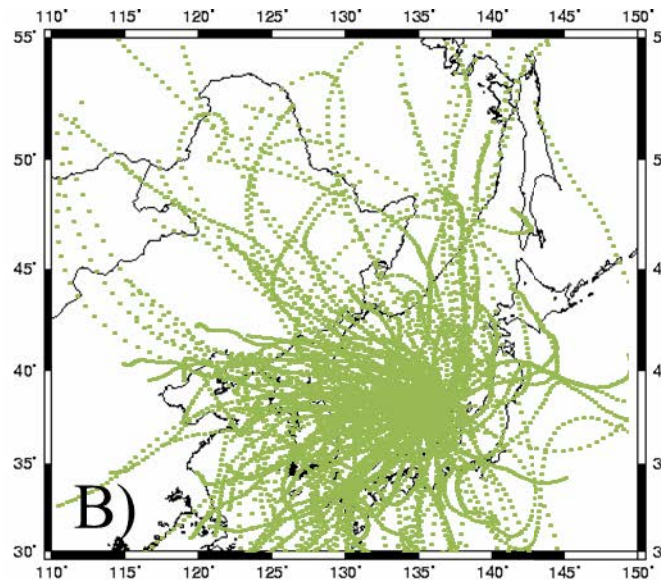
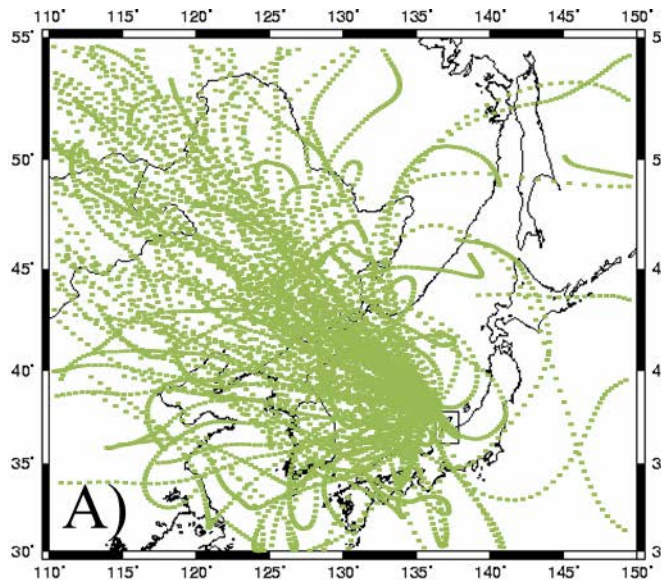
Fig. 2.



**Fig. 4.**



Latitude (deg)



Longitude (deg)



**Supplementary Material**

Factors affecting atmospheric 1-, 2-nitropyrenes and 2-nitrofluoranthene in winter at Noto peninsula,  
a remote background site, Japan

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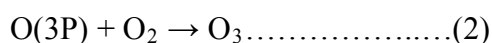
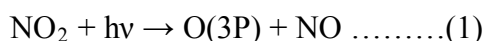
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## Section 1. Sampling design

It has been acknowledged that polycyclic aromatic hydrocarbon (PAH) and nitropolycyclic aromatic hydrocarbon (NPAH) can easily react with several oxidant reagents, such as O<sub>3</sub>, NO<sub>2</sub> and OH radical, in the atmosphere. Therefore, shorter sampling time (less than 24 hours) and use of the oxidant denuder are recommended although no oxidant denuder can completely remove all oxidant reagents in the atmosphere (EPA-454/R-02-011). However, as described in our previous report, the concentrations of total 9 PAHs (about 0.4 ng/m<sup>3</sup>; include Fluoranthene, Pyrene, Benz[*a*]anthracene, chrysene, benzo[*b*]fluoranthrene, benzo[*k*]fluoranthrene, benzo[*a*]pyrene, benzo[*ghi*]perylene and indeno[1,2,3-*cd*]pyrene) and TSP (about 10 μg/m<sup>3</sup>) were low in winter (Yang et al., 2007) and the result of our preliminary test showed that each NPAH could not be detected thoroughly by the 1 day sampling. This means that longer sampling time is necessary. Considering the artifact during sampling periods, we cited the data got from the Air Pollution Monitoring Car (APMC) which is installed in Monzen middle school about 10 km from our sampling site in 2004 (H 16 Annual of Ishikawa Prefectural Institute of Public Health and Environmental Science, 2005). The monitoring was carried out from July 5 to September 6 because the concentrations of air pollutants are higher in this period. As shown in Table SI-1, the average concentrations of SO<sub>2</sub>, NO, NO<sub>2</sub> and photochemical oxidant (mainly O<sub>3</sub>) were 0, 0, 2 and 39 ppb, respectively. The same monitoring results by APMC were also observed at Motor Sports Park which located about 2 km south of the Monzen middle school on Jun. 28 – Jul. 31, 2007 (H 19 Annual of Ishikawa Prefectural Institute of Public Health and Environmental Science, 2008). The O<sub>3</sub> levels were monitored only from 5:00 am to 8:00 pm. Since the duration of sunshine is long (Table SI-2) and the wind usually comes from inland (Fig. SI-2 A)) during this period, the O<sub>3</sub> at WAMS seems to be formed during transportation from inland as the following relationships (equation (1) and (2)):



Because of the shorter duration of sunshine (Table SI-2) and northwest wind (Fig. SI-2 B)) in winter, the concentrations of NO, NO<sub>2</sub> and O<sub>3</sub> might be lower in winter than in summer. Even if some of these oxidant reagents could transport from Northeast of China with PAH and NPAH in winter, most of them might be removed through the Japan Sea by rainout and washout effect.

Furthermore, Compared with Pyr and FR, BaP is the most reactive with all oxidants (Schauer et al., 2003; Tsapakis and Stephanou, 2003; Goriaux et al., 2006; Liu et al., 2006; Ringuet et al., 2012). According to these reports, if our sampling conditions bring larger artifact, the compositions of atmospheric PAHs in our sampling site should be significantly different than those in Northeast of China, such as in Shenyang. However, our previous data did not show that difference (Yang et al., 2007).

Therefore, we carried out a 7-day sampling design and evaluated our data observed only

evaluated our data in winter.

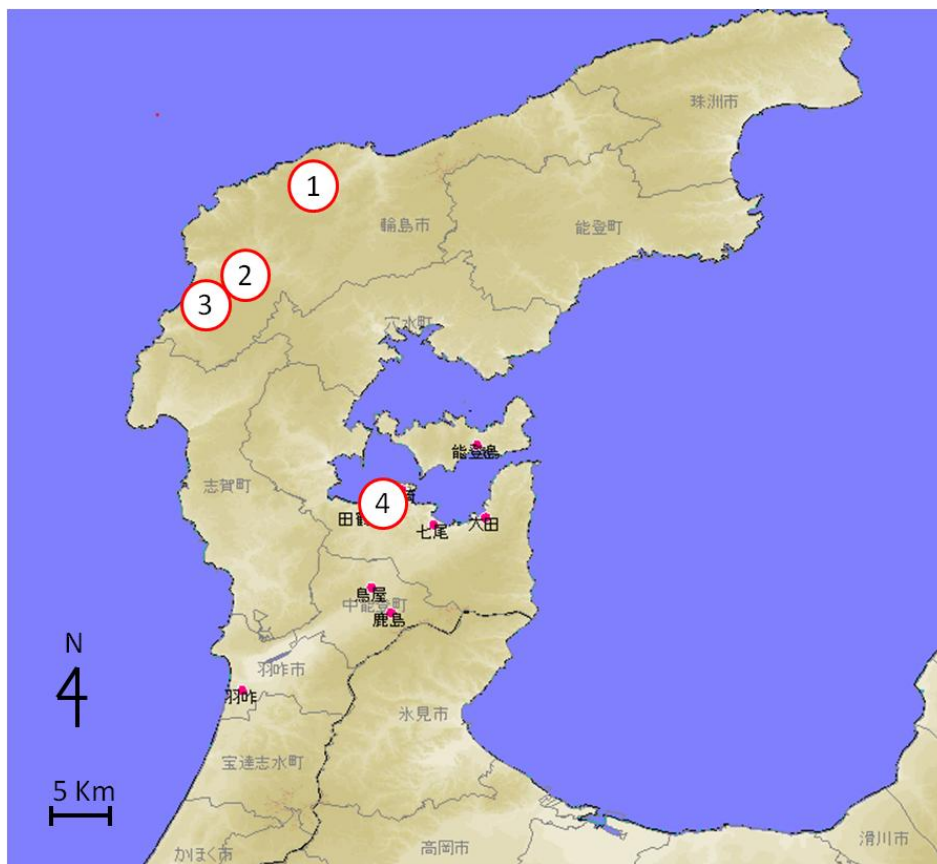


Fig. SI-1. Situation of our sampling site and other monitoring sites. (1): our sampling site. A background area. (2): Air Pollution Monitoring Car site in 2004. Monzen middle school, located at downtown in Monzen-Cho. (3) Air Pollution Monitoring Car site in 2007. Motor Sports Park, located at downtown in Monzen-Cho. (4): Air Pollution Monitoring Station. Tatsuruhama Station, located at downtown in Nanao city, about 50 km from our sampling site.

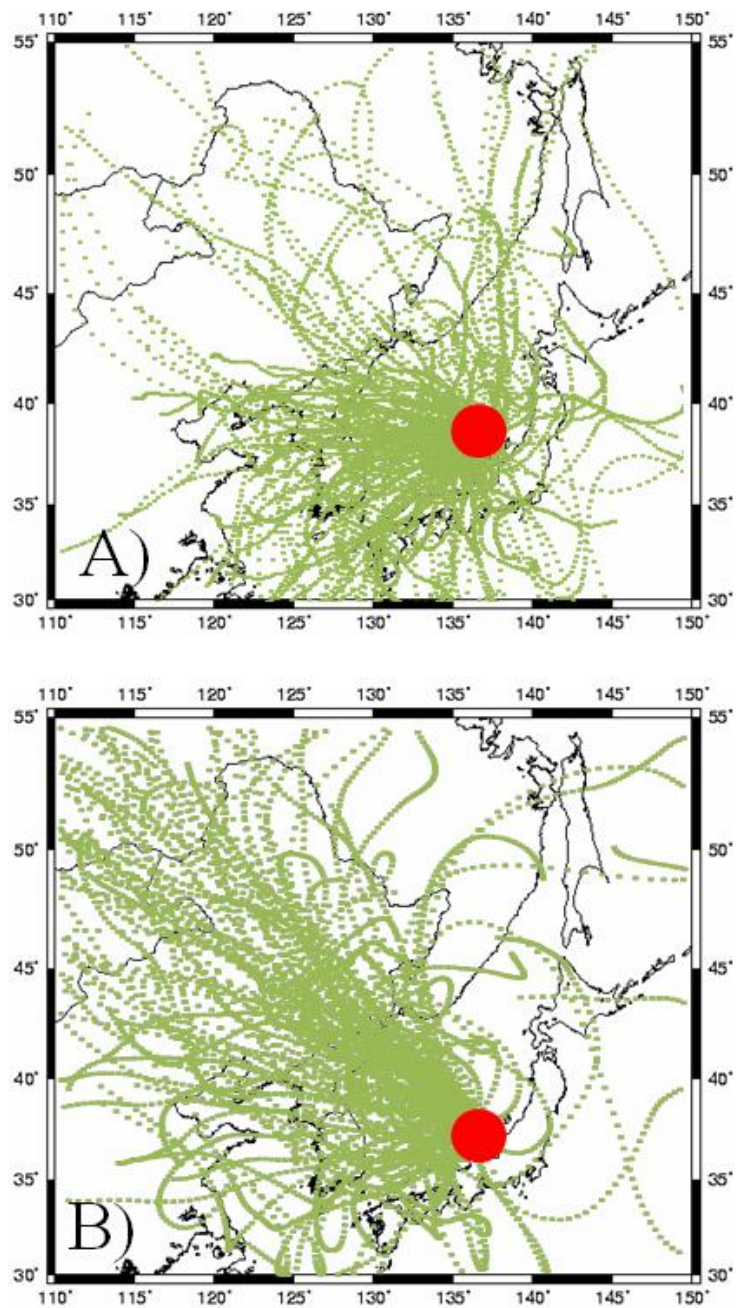


Fig. SI-2. Back trajectory analysis of air samples collected at our sampling sites by using METEX. A): May – Sep., 2006. B): Jan. – Apr., 2006.

Table SI-1 Average atmospheric concentrations of some gas reagents nearby our sampling site.

Site	Period	SO <sub>2</sub>	NO	NO <sub>2</sub>	O <sub>3</sub>
Monzen Middle School	Jul. 5 - Dec. 6, 2004	0.000	0.000	0.002	0.039
Monzen Motor Sports Park	Jun. 28 - Jul. 31, 2007	0.000	0.001	0.002	0.033
Unit: ppm.					

The detection limit of each pollutant is less than 1 ppb (twice the standard deviation of the noise).

Table SI-2 Monthly sunlight hours during our sampling period.

Month	Sunlight hour (h)			
	2004	2005	2006	2007
1	52	45	49	62
2	89	27	59	111
3	153	126	128	110
4	209	238	126	170
5	155	211	154	193
6	184	151	134	174
7	206	125	87	103
8	216	184	276	236
9	113	126	172	154
10	124	133	152	141
11	87	87	86	102
12	70	25	39	36

Data source: Japan Meteorological agency

(<http://www.jma.go.jp/jma/indexe.html>)

## Section 2. Analytical method of PAHs

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

Twenty microliter of the ethanol solution (2.3. *Sample preparation*) was injected into the HPLC with fluorescence detection (Tang et al., 2005). The system consisted of two HPLC pumps (LC-10A, Shimadzu, Kyoto, Japan), a fluorescence detector (RF-10A, Shimadzu), a system controller (SCL-10A, Shimadzu), an integrator (Chromatopac C-R7Ae, Shimadzu), a degasser (DGU-14A, Shimadzu), an auto sample injector (SIL-10A, Shimadzu), a column oven (CTO-10AS, Shimadzu), a guard column (Inertsil ODS-P, 4.0 i.d. x 10 mm, GL Sciences Inc., Tokyo, Japan) and an analytical column (Inertsil ODS-P, 4.6 i.d. x 250 mm, GL Sciences Inc.). The mobile phase was a mixture of acetonitrile and water with a gradient concentration mode of acetonitrile. The flow rate was 1 ml min<sup>-1</sup>. The time program of the fluorescence detector was set to detect at the optimum excitation and emission wavelengths for each PAH.

### Section 3. Weekly concentrations of PAHs and NPAHs at WAMS from Jan. 2006 to Dec. 2007

Month	Week	2-NFR	2-NP	1-NP	FR	Pyr	BaA	Chr	BbF	BkF	BaP	BgPe	IDP
Jan-06	1	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
	2	2.39	0.26	1.79	140	109	27.5	60.7	88.4	34.3	41.4	53.2	42.7
	3	2.57	0.30	1.66	267	205	55.1	118.0	111.0	42.9	57.2	93.9	57.8
	4	2.03	0.16	0.98	225	176	42.0	94.9	82.0	31.6	37.6	51.3	27.8
Feb-06	1	2.50	0.18	1.10	NA	NA	NA	NA	NA	NA	NA	NA	NA
	2	3.96	0.22	1.33	205	157	37.2	91.7	99.9	37.7	45.5	64.1	28.9
	3	3.31	0.16	0.88	116	90.0	21.7	54.6	61.9	22.7	28.6	42.3	18.0
	4	2.02	0.15	1.19	121	95.0	22.9	52.5	68.1	25.2	30.8	26.2	36.5
Mar-06	1	3.16	0.26	1.52	239	175	37.1	95.2	104	39.9	53.8	65.5	47.4
	2	2.27	0.12	0.65	152	115	24.3	64.7	71.9	27.4	37.8	47.7	40.3
	3	2.81	0.16	0.93	148	112	23.6	62.2	68.1	26.3	35.6	46.0	20.2
	4	2.13	0.17	0.78	180	136	30.6	76.5	82.5	32.5	45.8	52.9	41.3
	5	1.64	2.22	0.61	96.9	74.9	15.2	41.0	63.2	24.3	32.8	43.3	32.0
Apr-06	1	0.82	0.84	0.43	42.8	35.9	8.62	21.7	31.2	17.5	16.1	23.4	24.4
	2	4.48	0.38	0.73	116	83.1	14.8	54.3	90.6	66.5	40.8	55.3	48.2
	3	1.27	0.13	0.64	129	95.3	20.3	65.3	78.4	71.5	37.9	51.8	40.9
	4	2.07	0.17	0.37	113	81.5	15.5	55.2	63.7	87.2	38.0	51.0	32.9
May-06	1	0.52	0.03	0.30	33.5	23.7	5.99	14.8	54.5	29.4	35.4	45.4	32.6
	2	1.85	0.18	0.55	129	93.9	23.2	67.5	14.0	5.41	8.37	10.1	5.11
	3	0.81	0.09	0.19	42.2	35.1	8.90	24.1	44.0	18.2	27.9	31.5	26.3
	4	1.40	0.16	0.42	53.3	41.2	9.92	29.3	58.7	21.3	29.4	38.4	21.9
Jun-06	1	1.00	0.08	0.25	28.9	25.1	6.71	19.0	26.0	9.18	15.1	20.6	15.6
	2	0.17	ND	0.06	10.4	8.47	2.32	6.29	11.5	4.02	5.77	5.06	12.7
	3	1.55	0.16	0.34	NA	NA	NA	NA	NA	NA	NA	NA	NA
	4	1.48	0.16	0.31	43.8	38.9	8.14	27.3	51.6	19.6	27.8	33.0	21.3
	5	0.30	ND	0.10	14.9	11.8	2.80	8.19	11.5	4.99	7.02	7.55	6.07
Jul-06	1	1.89	0.19	0.22	24.8	18.7	5.97	16.0	41.0	14.5	20.9	26.6	21.0
	2	0.21	ND	0.10	13.1	9.2	2.18	5.76	11.6	3.76	5.27	5.66	7.64
	3	0.21	ND	0.09	14.0	15.0	4.05	10.4	14.1	6.36	8.19	11.3	11.0
	4	1.36	0.13	0.22	30.0	26.5	6.36	20.9	33.9	14.8	18.7	26.8	13.4
Aug-06	1	0.88	0.10	0.20	20.4	18.5	4.83	13.8	25.1	9.34	19.0	21.0	14.1
	2	0.30	0.07	0.11	13.8	13.9	3.70	10.6	19.4	8.16	12.3	17.0	14.0
	3	0.16	ND	0.08	12.6	13.1	3.29	9.20	15.8	5.94	8.97	10.7	12.3
	4	0.49	0.11	0.20	33.9	27.6	8.66	20.9	34.1	14.9	20.2	22.7	13.3
Sep-06	1	0.14	ND	0.05	12.8	12.4	3.43	7.82	12.1	4.89	1.17	9.60	13.1
	2	0.24	ND	0.07	17.1	16.3	4.60	10.4	15.6	6.82	8.64	12.0	13.2

	3	1.30	0.26	0.29	NA	NA	NA	NA	NA	NA	NA	NA	NA
	4	0.13	ND	0.05	NA	NA	NA	NA	NA	NA	NA	NA	NA
	5	0.38	ND	0.13	NA	NA	NA	NA	NA	NA	NA	NA	NA
Oct-06	1	0.99	0.09	0.80	34.7	27.1	8.52	22.9	29.8	11.4	19.1	29.8	21.0
	2	3.94	0.36	0.60	120	88.9	25.8	65.3	108	40.4	52.2	98.4	71.1
	3	0.34	0.05	0.12	37.4	27.8	7.04	17.5	30.9	12.0	15.9	30.6	20.2
	4	2.43	0.35	0.52	142	103	22.3	61.3	115	40.6	49.5	74.0	68.3
Nov-06	1	1.31	0.10	0.48	65.6	50.2	10.6	29.7	51.8	19.1	25.8	32.7	26.2
	2	1.95	0.18	2.52	154	114	23.8	60.2	121	41.3	53.3	70.3	59.8
	3	0.67	0.08	0.22	53.1	36.8	8.12	20.2	35.6	11.8	14.0	19.2	17.9
	4	2.09	0.11	0.63	79.5	60.4	14.3	32.4	58.0	19.8	23.5	34.5	32.6
Dec-06	1	4.16	0.34	0.94	282	133	38.9	89.9	131	44.9	48.2	57.2	75.5
	2	3.54	0.31	1.21	340	160	44.4	105.2	161	56.8	63.0	75.4	96.0
	3	1.72	0.15	0.65	179	76.0	20.0	54.7	92.2	31.1	34.2	44.3	50.5
	4	2.82	0.25	0.81	186	105	26.3	62.7	110	36.5	46.5	49.3	56.7
Jan-07	1	2.12	0.26	0.81	237	140	37.7	82.4	134	47.2	53.7	59.6	71.2
	2	1.78	0.29	0.89	232	137	29.7	79.0	125	41.8	45.9	57.0	65.2
	3	2.38	0.30	1.16	290	189	38.7	94.6	160	56.9	65.1	81.8	89.7
	4	1.18	0.08	0.48	188	86.1	23.5	56.4	56.2	19.4	20.3	23.6	29.0
Feb-07	1	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
	2	2.95	0.20	0.86	189	126	26.0	62.9	117	40.8	45.6	55.6	56.2
	3	2.32	0.16	0.68	117	78.0	15.8	41.8	62.2	21.7	24.3	50.5	36.2
	4	1.06	0.05	0.34	66.9	44.6	8.44	22.5	31.9	10.6	12.1	24.3	17.8
Mar-07	1	1.05	0.04	0.35	62.0	42.9	8.13	21.0	32.7	10.8	13.0	16.7	15.8
	2	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
	3	0.85	0.09	0.73	110	73.1	13.6	34.4	55.3	19.3	21.3	30.6	27.6
	4	2.32	0.29	0.69	161	106	19.9	60.2	101	34.8	43.7	60.8	58.2
	5	0.92	0.07	0.30	68.4	46.5	8.76	24.0	32.9	12.0	9.47	19.1	19.3
Apr-07	1	1.63	0.12	0.72	125	81.4	16.3	45.0	75.2	27.4	32.8	46.9	45.0
	2	0.19	0.02	0.09	9.01	6.8	1.28	3.68	5.37	1.80	2.47	3.64	3.13
	3	2.09	0.12	0.36	97.5	72.4	16.5	42.0	66.4	24.1	33.2	41.7	37.5
	4	2.86	0.26	0.84	189	133	24.5	78.0	139	50.1	61.6	91.5	90.9
May-07	1	2.42	0.34	0.75	193	135	24.8	87.4	140	50.8	61.3	93.1	89.1
	2	1.60	0.19	0.32	97.9	73.4	14.1	44.0	74.5	27.7	33.9	48.0	45.5
	3	0.95	0.09	0.36	66.3	49.4	9.32	33.6	54.3	18.2	23.3	32.0	31.8
	4	1.08	0.12	0.19	53.9	42.0	8.99	30.0	51.2	18.7	23.8	32.5	31.0
Jun-07	1	1.46	0.12	0.25	56.6	44.5	11.3	33.0	51.4	19.6	26.0	34.3	29.7
	2	0.69	0.06	0.14	24.4	20.3	4.91	15.4	23.4	8.79	12.3	15.9	12.6
	3	0.56	0.05	0.13	16.5	14.4	3.82	11.1	17.5	6.62	9.22	13.2	11.4



	4	0.49	0.04	0.10	13.1	10.7	3.05	9.43	14.8	5.63	6.14	10.6	8.54
	5	0.11	ND	0.07	5.94	5.73	1.78	3.67	6.00	2.40	3.39	4.96	4.24
Jul-07	1	0.19	0.03	0.05	7.19	6.17	1.99	5.05	8.45	3.26	4.56	6.37	5.10
	2	0.56	0.05	0.07	12.5	11.2	5.11	10.2	17.2	6.71	9.66	11.3	9.68
	3	0.42	0.05	0.08	34.7	28.4	7.59	15.7	33.6	13.0	12.3	21.5	21.3
	4	0.89	0.10	0.13	48.5	39.0	9.03	20.6	44.1	16.0	16.8	25.2	26.0
Aug-07	1	1.44	0.14	0.16	43.2	37.7	10.6	24.8	59.7	22.2	23.0	35.3	34.3
	2	0.75	0.09	0.14	35.1	40.9	7.24	19.6	56.3	20.0	21.3	30.4	25.3
	3	0.28	0.04	0.07	19.0	22.2	4.17	12.1	19.4	3.33	8.82	12.9	11.7
	4	0.15	0.04	0.05	16.9	20.6	3.49	11.5	21.5	8.03	9.08	14.3	12.6
	5	0.18	0.02	0.05	4.95	5.04	2.58	5.00	9.84	3.83	4.56	8.09	5.97
Sep-07	1	0.40	0.04	0.11	15.7	13.2	2.71	8.36	13.8	5.13	6.05	10.2	9.1
	2	1.17	0.10	0.16	20.0	20.0	8.66	16.8	33.3	13.8	21.4	28.6	17.6
	3	1.75	0.12	0.30	42.2	34.1	9.91	26.6	47.5	18.4	23.3	28.9	29.0
	4	0.25	0.06	0.11	35.0	26.6	5.31	16.5	30.5	10.4	12.1	18.7	17.8
Oct-07	1	0.62	0.10	0.12	54.6	40.8	9.30	27.8	43.3	15.7	20.3	25.6	25.3
	2	0.25	0.06	0.12	59.7	43.7	7.91	23.9	34.5	12.7	16.3	21.7	22.7
	3	1.68	0.20	0.31	103	74.2	15.9	52.8	92.1	31.4	35.5	55.4	51.6
	4	2.19	0.16	0.26	39.2	30.8	11.4	29.3	57.9	20.5	23.5	34.3	32.4
Nov-07	1	3.57	0.55	0.80	216	157	35.9	91.1	180	64.5	76.3	107	107
	2	2.15	0.32	0.69	176	120	26.2	71.4	134	45.6	53.2	74.2	69.8
	3	3.73	0.44	0.80	273	189	42.3	101	157	54.6	65.6	75.2	80.9
	4	3.47	0.41	0.93	248	177	39.4	103	195	67.3	83.2	105	99.1
	5	2.87	0.26	0.56	158	119	25.0	59.0	120	42.2	48.4	61.6	62.6
Dec-07	1	3.02	0.37	0.97	218	157	34.3	75.6	164	57.2	67.1	83.0	89.9
	2	5.12	0.58	1.41	404	275	58.6	138	222	73.7	86.2	99.4	115
	3	8.04	0.68	1.87	418	285	66.1	155	301	107	125	161	172
	4	2.69	0.29	1.05	183	126	31.7	75.6	138	46.5	51.1	61.6	65.9

Unit: pg/m<sup>3</sup>.

NS: no sample. ND: not detected. NA: not analyzed.

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