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Recent Changes in Atmospheric Polycyclic Aromatic Hydrocarbons and Nitropolycyclic Aromatic Hydrocarbons in Shenyang, China

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Key words: Polycyclic aromatic hydrocarbon, Nitropolycyclic aromatic hydrocarbon, 1-Ntropyrene/pyrene ratio ([1-NP]/[Pyr]), Air pollution, Shenyang government Blue Sky Project.

Abstract

Airborne particulates were collected in three size fractions by using Anderson low-volume air samplers in Shenyang, China in winter and summer in 2007. Compared with data obtained in 2001 at the same sites, the total concentrations of nine polycyclic aromatic hydrocarbons (PAHs) in winter decreased by 67% at one site and decreased by 40% at the other site, while the total concentrations of four nitropolycyclic aromatic hydrocarbons (NPAHs) did not decrease. This suggests that environmental countermeasures begun in 2001 were effective in decreasing the concentration of PAHs. However, in summer, the concentrations of PAHs and NPAHs rose by the factors of 4 and 5, respectively, possibly because of an increase in the number of motor vehicles.

Introduction

Many polycyclic aromatic hydrocarbons (PAHs) and nitropolycyclic aromatic hydrocarbons (NPAHs) are carcinogenic and/or mutagenic. The International Agency for Research on Cancer has ranked benzo[*a*]pyrene (BaP) in Group 1 (carcinogenic to humans) and 1-nitropyrene (1-NP) in Group 2A (probably carcinogenic to humans) (IARC, 2005). Several PAHs also have estrogenic/antiestrogenic or antiandrogenic activities (Kizu et al., 2000). Atmospheric PAHs such as BaP and NPAHs such as 1-NP mainly originate from imperfect combustion and pyrolysis of organic matters (Hayakawa et al., 1995a; Rogge et al., 1993). In addition, some NPAHs, such as 2-NP, are formed in the atmosphere via reactions of their parent PAHs and NO_2 (Arey et al., 1986). We previously reported that the main contributors to atmospheric PAHs and NPAHs were automobiles in Japanese and South Korean commercial cities (Sapporo, Kanazawa, Toyama, Tokyo and Seoul) (Kakimoto et al., 2000, 2002; Hayakawa et al., 2000, 2002; Tang et al., 2002a, 2005), while they were coal combustion systems in Chinese and Far-eastern Russian cities (Beijing, Shenyang, Fushun, Tieling and Vladivostok) (Hattori et al., 2007; Hayakawa et al., 2007; Tang et al., 2002a, 2005, 2009).

During the past three decades, large increases in the consumption of petroleum and coal in China have led to air pollution. Shenyang city is the economic center of northeast China. The main sources of air pollution in Shenyang are exhausts from domestic heating, industry and motor vehicles. In 2001 - 2002, the average concentrations of total PAHs (9 kinds of PAHs) and NPAHs (7 kinds of NPAHs) in Shenyang were 534 pmol m^{-3} and 677 fmol m^{-3}, respectively (Hattori et al., 2007). These concentrations were significantly higher than those in Kanazawa, Japan in the same period. To reduce air pollution, the Shenyang government undertook the Blue Sky Project (*http://www.syepb.gov.cn/*), in which 100 factories were transferred to the outer city, and 5,000 inefficient boilers for domestic heating were removed between 2001 to 2007. These changes helped to reduce the annual average concentrations of PM_{10} from 190 μg m^{-3} in 2001 to 120μg m^{-3} in 2009 (*http://www.syepb.gov.cn/*).

In this study, airborne particulates (APs) were collected by using the same method and at the same sites as our previous investigation in 2007 (Hattori et al., 2007). Our objectives were to clarify the effect of the above countermeasures and to understand the present pollution status of PAHs and NPAHs in Shenyang, China.

Materials and Methods

Sampling Sites

Sampling sites in this study were the same as our previous study (Hattori et al., 2007). SY-1 (Heping elementary school) was in a commercial area and SY-2 (Taishan elementary school) was in a mixed residential and commercial area. Airborne particulates were collected simultaneously at the two sites using Andersen low-volume air samplers (AN-200, Shibata Sci. Tech., Tokyo, Japan) at a flow rate of 28.3 L min^{-1}. The height of the intake varied from 1 to 3 m above ground level. APs were separately collected only in three fractions according to their aerodynamic size: larger than 7 μm, 2.1 ~ 7 μm and smaller than 2.1 μm onto quartz fiber filters (2500QAT-UP, Pallflex Products, Putnam, CT, U. S. A.) different to our previous study (Hattori et al., 2007; APs were collected in nine fractions and separated in same three granulometric groups for PAHs and NPAHs analysis). Air samples were collected at two sites on March 10 - 17 (winter) and September 17 - 24, 2007 (summer). Filters were replaced every day. At each site, seven 3-layer filters were used for each of the above sampling periods. The filters were dried in a desiccator in the dark, weighed and stored at -20°C until use.

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). 1-NP, 6-nitrochrysene (6-NChr), 6-nitrobenzo[*a*]pyrene (6-NBaP) and an internal standard for NPAHs (2-fluoro-7-nitrofluorene (FNF)) were purchased from Chiron AS (Trondheim, Norway). All other chemicals used were of analytical reagent grade.

Sample Treatment and Analytical Procedures

Three-layer filters (larger than 7 μm, 2.1 ~ 7 μm, smaller than 2.1 μm) of each sample were cut into small pieces and placed in a flask, respectively. By this treatment, the concentrations of PAHs and NPAHs in the three groups were obtained for each sample. Both PAHs and NPAHs were extracted ultrasonically twice with benzene/ethanol (3:1, v/v) and then the solution was filtered with a 0.45μm membrane filter (HLC-DISK13, Kanto Chemical CO.,INC., Tokyo, Japan). Internal standards, Pyr-d_{10}, BaP-d_{12} and FNF, were added to the flask prior to the ultrasonic extraction. In the case of PAHs, the filtrate was evaporated to dryness. The residue was dissolved in 0.5 mL of acetonitrile, and then injected into the HPLC system for PAHs. In the case of NPAHs, the filtrate was washed once with 5% (w/v) sodium hydroxide solution, once 20% (v/v) sulfuric acid solution and twice water for removing acid and base substance. Then the solution was evaporated to dryness with rotation evaporator. The residue was dissolved in 1 mL of 75% ethanol-0.02 M acetic acid-sodium acetate buffer (pH 5.5). The solution was filtered with a 0.45 μm HLC-Disk membrane filter (Kanto Chemical Co., Inc., Tokyo, Japan), and an aliquot of this solution was injected into the HPLC system for NPAHs. Other conditions were the same as in our previous reports (Hayakawa et al., 1991; Tang et al., 2002b).

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., 2002b).

The four NPAH species were determined by using HPLC with chemiluminescence detection. The HPLC system consisted of two reversed-phase columns (Cosmosil 5C18-MS, 4.6 i.d. x (250 + 150) mm, Nacalai Tesque, Tokyo, Japan) connected in series with chemiluminescence detection. The mobile phase was 10 mM imidazole buffer (pH 7.6)-acetonitrile (1:1, v/v), and the chemiluminescence reagent solution was an acetonitrile solution containing 0.02 mM bis(2,4,6-trichlorophenly)oxalate and 15 mM hydrogen peroxide. The flow rate was 1 mL min^{-1} for each solution. Other conditions were the same as in our previous report (Hayakawa et al., 1991; Tang et al., 2003).

Data Analysis

The major sources of PAHs and NPAHs were identified by a cluster analysis with Ward's method and standardized squared Euclidean distance. The statistical analysis software program used in this study was kindly provided by Dr. Susumu Hayakari of Aomori Prefectural Institute of Public Health and Environment (Aomori, Japan). For the cluster analysis, we used the concentration ratios of 1-NP to Pyr, 6-NBaP to BaP and individual PAH to total PAHs in the airborne particulates collected at two sites in 2001 - 2002 (Hattori et al., 2007) and 2007. The data of Tokyo in summer in 2004 and in winter in 2005 were used grouping (Tang et al., 2005). The data of average temperature, dew point and wind speed in Shenyang during our sampling periods were obtained from USA National Climatic Data Center (*http://lwf.ncdc.noaa.gov/oa/climate/onlineprod/drought/xmgr.html#gr*) and average humidity were calculated by using the data of average temperature and dew point.

Results and Discussion

Concentrations

The PAH and NPAH concentrations were higher in winter than in summer at each site and they were both higher at SY-1 than at SY-2 (Table 1). Measurements made in 2001 to 2002 showed similar increases in winter (Hattori et al., 2007).

Fig. 1 compares the total concentrations of nine PAHs and three NPAHs measured in the two studies (One of NPAHs measured in the present study was not measured in the earlier study). In winter, the concentrations of PAHs decreased by 40% at SY-1, which is in a commercial area, and decreased by 67% at SY-2, which is in a more residential area (Fig. 1A). However, the concentration of NPAHs did not change markedly at either site, which suggests that Shenyang's Blue Sky Project was more effective against PAHs than NPAHs in winter. On the other hand, in summer, the concentrations of PAHs and NPAHs rose by a factor of at least 4 at both sites. A likely contributing factor was an increase in the number of motor vehicles from 360,000 in 2000 to 560,000 in 2007 (http://www.syepb.gov.cn/).

Distribution of PAHs, NPAHs and APs in Different Size Particulate Fractions

The concentrations and compositions of air pollution matters are often affected by meteorological conditions (Yamasaki et al., 1982). PAH, NPAH and AP concentrations were found to be highly correlated with humidity at the two sites in summer (Table 2). However, no such correlations were found with temperature or wind speed, possibly because of their smaller ranges (15 - 22°C and 1.3 - 2.4 m s^{-1}) and because rainfall was only one-third the normal amount during the summer sampling period. However, in winter, AP (> 7 μm) was negatively correlated with humidity and positively correlated with wind speed at both sites. Temperature also seemed to be positively correlated with PAH and NPAH levels in all size fractions. These observations suggest that cold and dry air, which blows predominantly from the inner Asian continent in winter, increased the concentrations of coarse particulates (> 2.1 μm) and decreased the concentrations of PAHs, NPAHs and fine particulates (< 2.1 μm) in the atmosphere (Table 2).

The main sources of atmospheric PAHs and/or NPAHs in Shenyang in summer are automobiles, while in winter they seem to be coal stoves and coal boilers used for domestic heating (Tang et al., 2005; Hattori et al., 2007; Kong et al., 2010). In 2007, the percentages of total PAHs and NPAHs in the fine particulate fraction, which is the fraction that most adversely affects human health, were about 92% and 81%, respectively at both sites (Fig. 2), in agreement with previous reports. (Hayakawa et al., 1995b; Kawanaka et al., 2004). However, in 2002, the percentages of total PAHs and total NPAHs in the fine fraction were 70% and 60% of the total, respectively. In winter 2002, the coarse size particulates had high PAH and NPAH levels (Fig. 2). In general, inefficient boilers contributed greatly to the large size particulates in the atmosphere because of their imperfect combustion. Therefore, the increase in the ratio of the total PAHs and total NPAHs in the fine fraction from 2002 to 2007 was probably due to the removal of about 5000 boilers by the Shenyang government.

However, the difference of atmospheric concentrations of NPAHs between 2002 and 2007 was not significant. According to our previous study, the concentrations of NPAHs in the particulates collected in automobiles were significantly higher than those in coal combustion systems. By contrast, the concentrations of PAHs were lower in automobiles (Hayakawa et al., 2000; Tang et al., 2005). In addition, the particulate sizes originating from automobiles were very small (Ho et al., 2006). These observations suggest that the increase in the number of motor vehicles also contributed to the fine particulate fractions of PAHs and NPAHs, especially the latter.

Compositions and Main Sources

Multivariate statistical analysis methods and several diagnostic ratios have been used to identify possible emission sources of PAHs and NPAHs and to compare their compositions in the atmosphere (Bourotte et al., 2005; Kakimoto et al., 2002; Rogge et al., 1993). The compositions of PAHs and NPAHs were compared by a cluster analysis using Ward's method. As parameters, we used the concentration ratios of 1-NP to Pyr, 6-NBaP to BaP and individual PAHs to total PAHs in the airborne particulates collected at the two sites in 2001 - 2002 and 2007. The same compound pairs were investigated in Tokyo in summer in 2004 and in winter in 2005 (Tang et al., 2005) and are used here as a reference. As shown in Fig. 3, two large clusters were observed according to the compositions of PAHs and NPAHs at all sites. Cluster 1 includes all winter samples collected at the two sites in Shenyang. All summer samples collected at the two sites in Shenyang and summer and winter samples in Tokyo were grouped into Cluster 2. This result indicates that the compositions of PAHs and NPAHs in winter were different from the compositions in summer at the two sites in Shenyang and that the compositions of PAHs and NPAHs in summer at these sites were similar to those in Tokyo in both summer and winter. Previously, we reported that the main sources of atmospheric PAHs and NPAHs were motor vehicles in all seasons in Tokyo, while they were coal combustion systems in winter and motor vehicles and coal combustion systems in summer in Shenyang (Tang et al., 2005; Hattori et al., 2007). These results suggest that the major contributors of atmospheric PAHs and NPAHs in Shenyang did not change significantly during 2001 - 2002 to 2007. However, the data in Cluster 1 in Fig. 3 indicate that the compositions of PAHs and NPAHs in winter at the two sites in Shenyang slightly differed between 2002 and 2007. Possible causes of the differences in 2007 include the air pollution countermeasures and the increase in the number of vehicles.

The [1-NP]/[Pyr] ratio is a useful indicator for estimating the contributions of motor vehicles and coal combustion systems to atmospheric PAHs and NPAHs (Tang et al., 2005). Although 1-NP can form during the sampling and a part of Pyr is distributed in the gas phase, the yields of 1-NP that formed in the filter were smaller than 5% and the partition ratios in the gas and particulate phases of Pyr depend on temperature (Nielsen, 1983; Yamasaki et al., 1982). Figure 4 shows the [1-NP]/[Pyr] ratios in the atmospheric particulates collected at the two sites of Shenyang in 2001 - 2002 and 2007. During the intervening 5 years, the [1-NP]/[Pyr] ratios in winter increased from 0.003 to 0.014 at SY-1 and from 0.002 to 0.010 at SY-2. In summer, the [1-NP]/[Pyr] ratios also increased from 0.008 (2001) to 0.025 (2007) at SY-1. Although no data was obtained at SY-2 in summer 2001, the [1-NP]/[Pyr] ratio was very high (0.025) as well. Furthermore, the [1-NP]/[Pyr] ratio variance at SY-1 was larger in summer than in winter. The [1-NP]/[Pyr] ratio of particulates emitted by coal combustion systems (0.001) was much smaller than the ratio of particulates emitted by diesel-engine automobiles (0.36) (Tang et al., 2005). These results suggest that motor vehicles became one of the major contributors of atmospheric PAHs and NPAHs in Shenyang in 2007 not only in summer but also in winter.

Conclusions

The concentrations and distribution of PAHs and NPAHs in different particulate size fractions changed between 2001 - 2002 and 2007. In winter, the concentrations of coarse size particulates (> 2.1 μm) in the atmosphere decreased from 57.5% to 44.6% over the 5-year period. Concurrently, the concentrations of atmospheric PAHs and NPAHs in winter in the coarse size particulate fractions, which might have originated from inefficient boilers, decreased from 0.35 pmol μg^{-1} to 0.15 pmol μg^{-1}, and 0.55 fmol μg^{-1} to 0.32 fmol μg^{-1}, respectively, during the 5 years. Especially, the concentrations of PAHs and NPAHs in winter 2007 decreased significantly from the concentrations in winter 2002, probably largely as a result of Shenyang's Blue Sky Project. However, both PAH and NPAH concentrations in summer increased from 2001 to 2007, and the concentrations of NPAHs in winter did not change markedly between 2002 and 2007. Our comparative data on the particulate distributions, seasonal variations and compositions of PAHs and NPAHs in the atmosphere show that motor vehicles have become one of the major contributors of atmospheric PAHs and NPAHs in Shenyang not only in summer but also in winter.

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Figure Captions

Figure 1. Comparison of atmospheric PAHs and NPAHs at two sites in Shenyang in 2001 - 2002 and in 2007. Each bar means the average concentration of total PAHs or NPAHs; PAHs includes FR, Pyr, BaA, Chr, BbF, BkF, BaP, BgPe and IDP; NPAHs includes 1-NP, 6-NC and 6-NBaP. The data of Shenyang in 2001 - 2002 are from Hattori et al., 2007.

Figure 2. Particulate partitions of PAHs, NPAHs and APs in three size fractions at two sites in Shenyang in 2001 - 2002 and in 2007. Three size fractions mean larger 7 μm, 7 - 2.1 μm and smaller than 2.1 μm. The data of Shenyang in 2001 - 2002 referenced from Hattori et al., 2007. The concentrations of PAHs, NPAHs and APs in each particulate size fraction are shown within each box.

Figure 3. Cluster analysis dendrogram of atmospheric PAHs and NPAHs at two sites in Shenyang and in Tokyo by using Ward's method and standardized squared Euclidean distance. The parameters used for the cluster analysis were the concentration ratios of 1-NP to Pyr, 6-NBaP to BaP and individual PAH to total PAHs in the airborne particulates collected at two sites in 2001 - 2002 and 2007.

Figure 4. Comparison of [1-NP]/[Pyr] ratios at two sites in Shenyang. The data of Shenyang in 2001 - 2002 are from Hattori et al., 2007.

Table 1 Atmospheric concentrations of nine PAHs and four NPAHs in 2007 at two sites in Shenyang, China.

		Summer		Winter	
		SY-1	SY-2	SY-1	SY-2
PAH	FR	7.97 ± 3.55	7.22 ± 3.33	67.9 ± 36.0	51.6 ± 26.7
(pmol m^{-3})	Pyr	6.99 ± 2.60	6.41 ± 2.63	70.1 ± 34.8	60.3 ± 31.8
	BaA	7.11 ± 3.63	5.41 ± 2.94	63.1 ± 28.2	57.9 ± 35.2
	Chr	13.4 ± 7.52	9.91 ± 6.19	79.8 ± 34.3	67.5 ± 34.0
	BbF	34.3 ± 28.5	28.7 ± 27.9	69.9 ± 32.9	61.8 ± 32.4
	BkF	11.2 ± 8.66	9.71 ± 8.62	26.5 ± 11.9	24.9 ± 12.6
	BaP	11.4 ± 6.45	10.2 ± 6.70	44.1 ± 19.3	42.9 ± 22.1
	BgPe	24.6 ± 13.8	23.1 ± 14.9	46.0 ± 17.1	56.2 ± 26.5
	IDP	14.4 ± 8.57	14.6 ± 10.0	22.2 ± 9.24	27.5 ± 13.1
	Total PAHs	131 ± 80.2	115 ± 79.6	491 ± 215	451 ± 226
NPAH	9-NA	718 ± 400	600 ± 369	5400 ± 3280	5430 ± 3210
(fmol m^{-3})	1-NP	159 ± 49.8	147 ± 54.7	857 ± 459	555 ± 184
	6-NC	205 ± 100	191 ± 86.0	544 ± 260	343 ± 157
	6-NBaP	31.9 ± 15.6	32.4 ± 14.6	116 ± 58.5	93.4 ± 64.1
	Total NPAHs	1110 ± 526	972 ± 493	6910 ± 3450	6420 ± 3410

All data represent mean ± S.D., n = 7.

Table 2 Correlation coefficients between PAHs, NPAHs and APs in different particulate fractions and several meteorological conditions.

		Winter			Summer		
		Temperature (°C)	Wind speed (m s^{-1})	Humidity (%)	Temperature (°C)	Wind speed (m s^{-1})	Humidity (%)
Meteorological Condition	Wind speed (m s^{-1})	-0.58			-0.71		
	Humidity (%)	0.27	-0.81*		-0.63	0.19	
SY-1	PAHs (> 7 μm)	0.24	-0.64	0.79*	0.20	0.12	-0.83**
	PAHs (7 - 2.1 μm)	0.54	-0.74	0.82**	0.04	0.31	-0.75*
	PAHs (< 2.1 μm)	0.43	-0.81*	0.92**	-0.11	0.56	-0.63
	NPAHs (> 7 μm)	0.41	-0.47	0.37	0.18	-0.18	-0.73
	NPAHs (7 - 2.1 μm)	0.61	-0.65	0.50	0.03	-0.02	-0.67
	NPAHs (< 2.1 μm)	0.27	-0.63	0.70	0.13	0.18	-0.82**
	APs (> 7 μm)	-0.49	0.90**	-0.84**	0.04	-0.04	-0.63
	APs (7 - 2.1 μm)	-0.11	0.70	-0.58	-0.05	-0.04	-0.55
	APs (< 2.1 μm)	0.76	-0.64	0.57	-0.20	0.14	-0.49
SY-2	PAHs (> 7 μm)	0.48	-0.81*	0.83**	0.21	0.07	-0.84**
	PAHs (7 - 2.1 μm)	0.62	-0.77*	0.61	0.09	0.17	-0.76*
	PAHs (< 2.1 μm)	0.34	-0.77*	0.79*	-0.14	0.57	-0.52
	NPAHs (> 7 μm)	0.42	-0.75*	0.73	0.34	0.05	-0.88**
	NPAHs (7 - 2.1 μm)	0.66	-0.92**	0.76*	0.16	0.21	-0.79*
	NPAHs (< 2.1 μm)	0.63	-0.87**	0.79*	0.18	0.10	-0.86**
	APs (> 7 μm)	-0.39	0.90**	-0.90**	0.47	-0.21	-0.90**
	APs (7 - 2.1 μm)	-0.00	0.50	-0.62	0.18	0.01	-0.79*
	APs (< 2.1 μm)	0.68	-0.66	0.53	-0.04	0.19	-0.61

n = 7. The data of average temperature, dew point and wind speed in Shenyang during the sampling periods were obtained from USA National Climatic Data Center (*http://lwf.ncdc.noaa.gov/oa/climate/onlineprod/drought/xmgr.html#gr*) and average humidity were calculated by using the data of average temperature and dew point.

Fig. 1

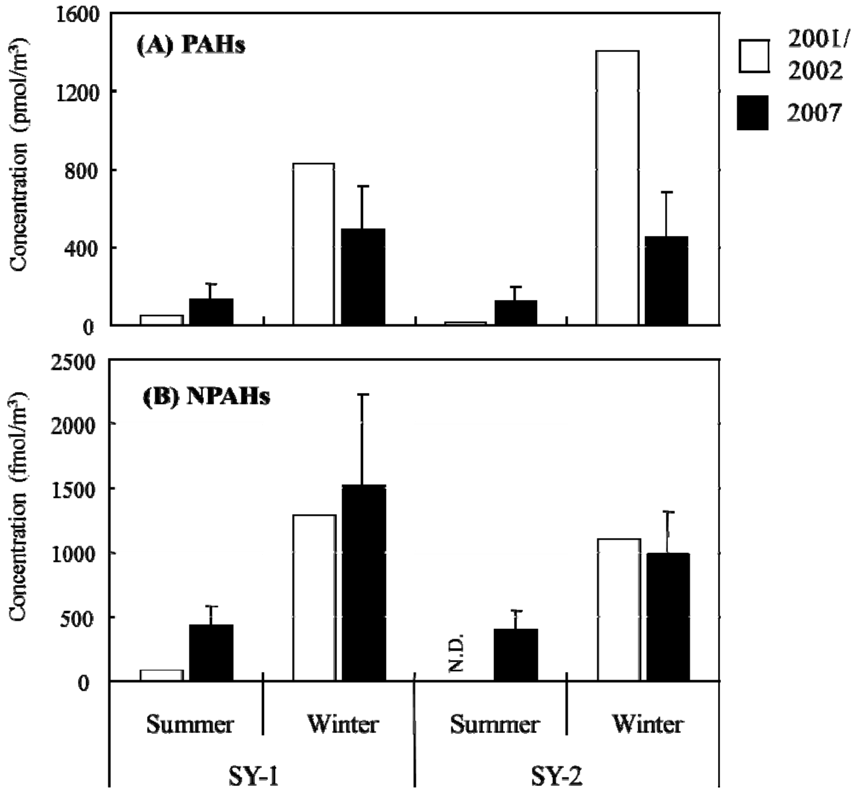

(A) PAHs
Concentration (pmol/m^3)
1600
1200
800
400
0
(B) NPAHs
Concentration (fmol/m^3)
2500
2000
1500
1000
500
0
N.D.
□ 2001/2002
■ 2007
Summer
Winter
Summer
Winter
SY-1
SY-2

Fig. 2

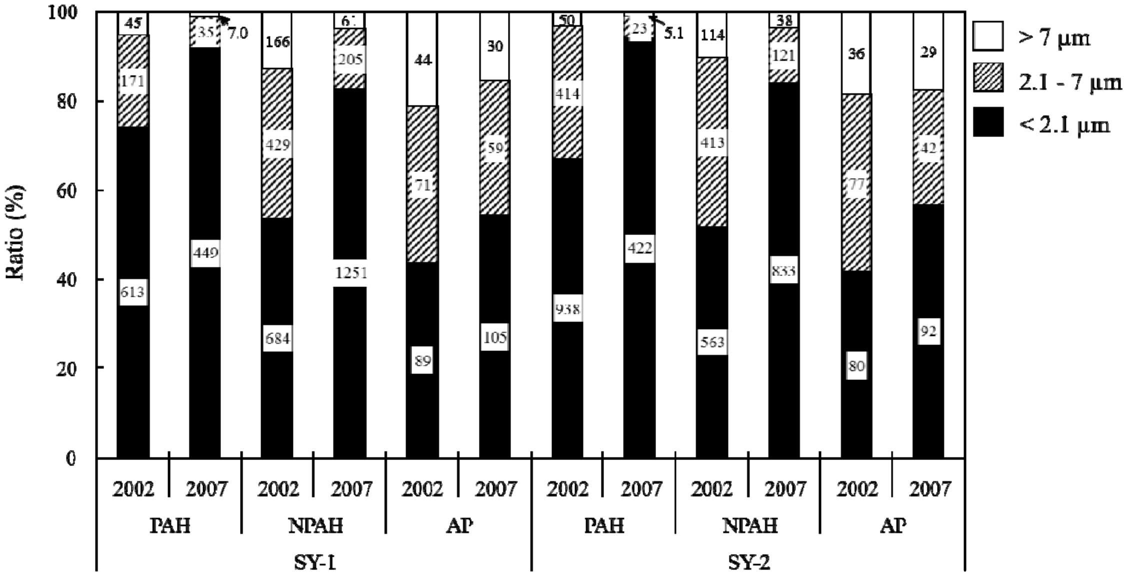

100
80
60
40
20
0
Ratio (%)
45
171
613
35
7.0
449
166
429
684
6
205
1251
44
71
89
30
59
105
50
414
938
23
5.1
422
114
413
563
38
121
833
36
77
80
29
42
92
2002
2007
2002
2007
2002
2007
2002
2007
2002
2007
2002
2007
PAH
NPAH
AP
PAH
NPAH
AP
SY-1
SY-2
> 7 µm
2.1 - 7 µm
< 2.1 µm

Fig. 3

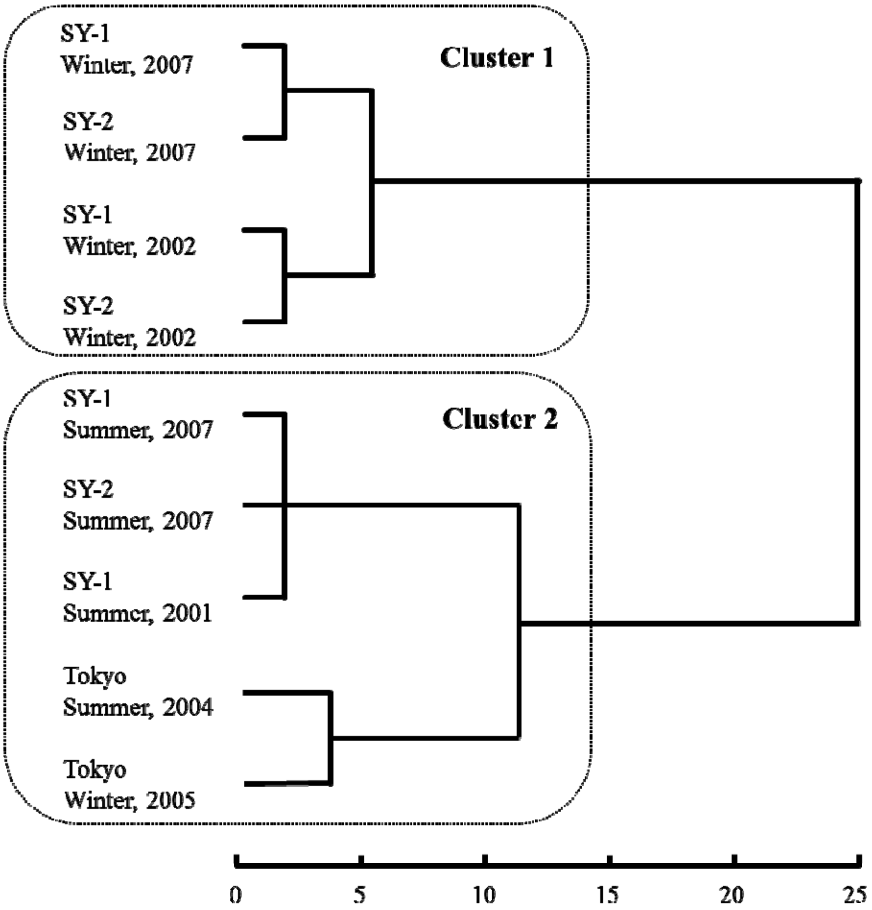
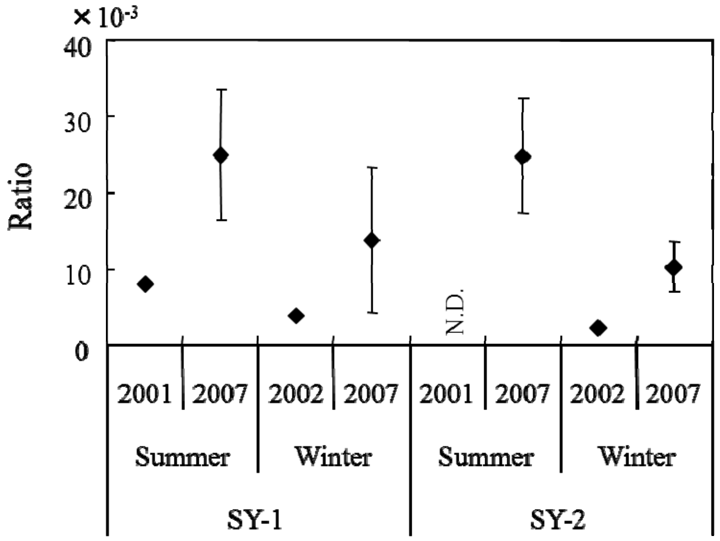

SY-1
Winter, 2007
SY-2
Winter, 2007
SY-1
Winter, 2002
SY-2
Winter, 2002
Cluster 1
SY-1
Summer, 2007
SY-2
Summer, 2007
SY-1
Summer, 2001
Tokyo
Summer, 2004
Tokyo
Winter, 2005
Cluster 2
0
5
10
15
20
25

Fig. 4


×10-3
40
30
20
10
0
Ratio
N.D.
2001
2007
2002
2007
2001
2007
2002
2007
Summer
Winter
Summer
Winter
SY-1
SY-2