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Atmospheric Behaviors of Polycyclic Aromatic Hydrocarbons and Nitropolycyclic Aromatic Hydrocarbons in East Asia

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ABSTRACT

Hazardous polycyclic aromatic hydrocarbons (PAHs) and nitropolycyclic aromatic hydrocarbons (NPAHs) are mainly originated from imperfect combustion of fossil fuels such as petroleum and coal. The consumptions of not only petroleum but also coal have been increasing in the East Asian countries. This review describes the result of international collaboration research concerning characteristics and major contributors of atmospheric PAHs and NPAHs in cities in Japan, Korea, China and Russia. We collected airborne particulates in ten cities in the above countries and six PAHs and eleven NPAHs were determined by HPLC methods using fluorescence and chemiluminescence detections. The total PAH concentrations were much higher in Chinese cities (Fushun, Tieling, Shenyang and Beijing) than those in other cities (Vladivostok, Busan, Kanazawa, Kitakyushu, Sapporo and Tokyo). The total NPAH concentrations were also higher in Chinese cities than those in the other cities. The [NPAH]/[corresponding PAH] ratios are much larger in diesel-engine exhaust particulates than those in coal-burning particulates. The [1-nitropyrene]/[pyrene] ratio of airborne particulates was much smaller in the four Chinese cities, suggesting that coal combustion systems such as coal heaters were the main contributors. On the other hand, the ratios were larger in Korean and Japanese cities, suggesting the large contribution of diesel-engine vehicles.

Key words: Polycyclic aromatic hydrocarbon, Nitropolycyclic aromatic hydrocarbon, East Asia, Long range transport, Airborne particulate

1. INTRODUCTION

Several polycyclic aromatic hydrocarbons (PAHs) and nitropolycyclic aromatic hydrocarbons (NPAHs) are carcinogenic and/or mutagenic. International Agency for Research on Cancer (IARC) has already ranked 1, 6-, 1, 8-dinitropyrene (1, 6-, 1, 8-DNPs), 1-, 4-nitropyrene (1-, 4-NPs) and 6-nitrochrysene (6-NC) in group 2B (possibly carcinogenic to humans) (IARC, 1996). Benzo[*a*]pyrene (BaP) which is a typical carcinogenic PAH has been considered as a cause of lung cancer (Epstein *et al.*, 1979). Furthermore, in recent years, we have found that several PAHs and NPAHs also had estrogenic/antiestrogenic and antiandrogenic activities (Hirose *et al.*, 2001; Kizu *et al.*, 2000).

PAHs and NPAHs are mainly originated from imperfect combustion of organic matters such as coal and petroleum. Both PAHs having 4 rings or more and NPAHs are detected in particulates exhausted from diesel- and gasoline-engine vehicles, while PAHs of lower molecular weights (3 rings or below) were detected in the gaseous phase in the atmosphere and unburned diesel fuel(Oda *et al.*, 2001; Gratz *et al.*, 2000; Hayakawa *et al.*, 2000; Marr *et al.*, 1999; Masclet *et al.*, 1986; Tokiwa and Ohnishi, 1986). PAHs and NPAHs were also detected in smoke from steel and iron industries(Yang *et al.*, 2002). In addition to the NPAHs such as 1, 3-, 1, 6-, 1, 8-DNPs and 1-NP that are emitted directly from the above sources, other important sources of NPAHs such as 2-NP and 2-nitrofluoranthene (2-NFR) are heterogeneous or homogeneous reactions of parent PAHs with nitrogen oxides (NO_x) and hydroxyl (OH) radicals in the atmosphere (Pitts *et al.*, 1985).

On the other hand, about 60% of the earth's population is in Asia over 26% of the earth's population lives in East Asian countries, Japan, China, North and South Korea, Mongolia and Russia surrounding the Japan Sea. These countries' primary energy consumption accounts for more than 26% of the global primary energy consumption. However, there are great differences in the type of energy consumption, depending on the country. Sixty-eight percent of China's primary energy is coal, but in Japan and South Korea, oil has the biggest share, at 49-50%, with coal account-

ing for 22-24%. On the other hand, 54% of Russia's primary energy is natural gas (BP Statistcal Report, 2004). The combustion of these fossil fuels produces and releases not only CO_2, but also many types of hazardous substances that are a major cause of atmospheric pollution. The concentrations and composition of these hazardous substances in the atmosphere vary greatly depending on energy status and the traffic and

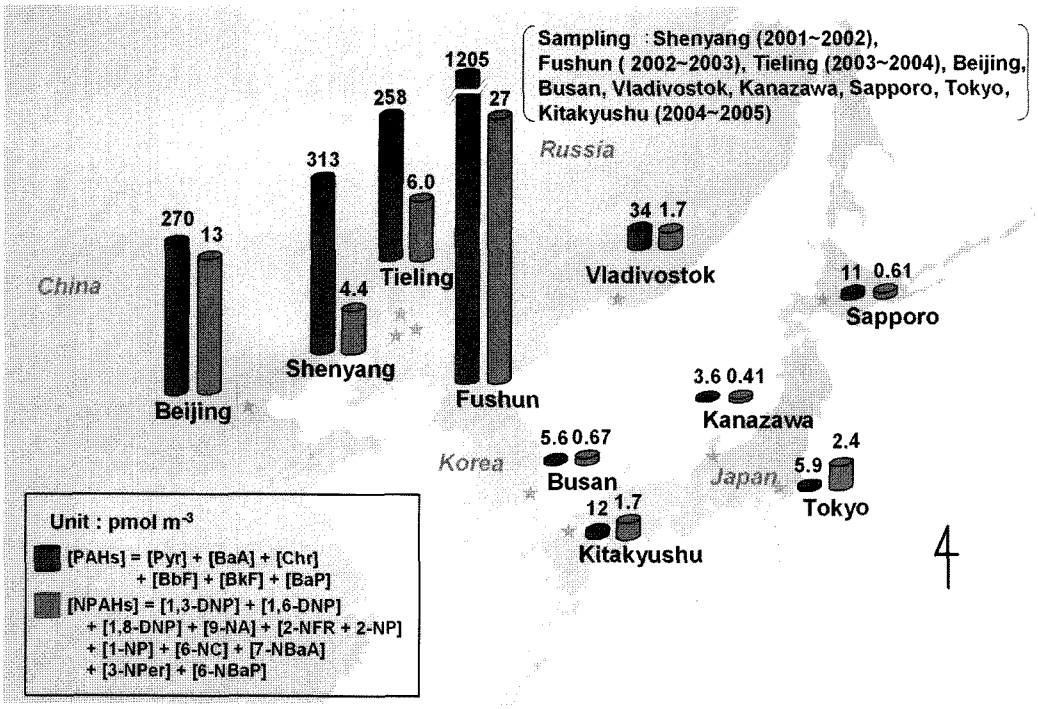

Fig. 1. Annual average concentrations of PAHs and NPAHs in East Asian cities.

Table 1. Concentrations of PAHs and NPAHs in the atmosphere collected in Fushun and Kanazawa in winter and summer.

Compound	Fushun		Kanazawa	
	Winter (n=3)	Summer (n=3)	Winter (n=28)	Summer (n=23)
PAH (pmol m^{-3})				
Pyr	483±147	40±8.6	0.74±0.61	0.56±0.27
BaA	233±11	48±7.3	0.48±0.24	0.27±0.11
Chr	246±16	143±50	0.79±0.40	0.44±0.18
BbF	205±22	225±70	0.76±0.39	1.2±0.74
BkF	74±8	69±20	0.37±0.20	0.51±0.32
BaP	138±13	62±12	0.64±0.41	0.46±0.26
Total	1379±180	587±168	3.8±2.1	3.4±1.6
NPAH (fmol m^{-3})				
1,3-DNP	6.3±2.2	52±3.0	0.33±0.29	0.47±0.54
1,6-DNP	29±10	174±19	0.83±1.1	0.71±0.73
1,8-DNP	26±13	5.2±1.6	2.1±2.8	3.6±3.9
9-NA	1246±340	1966±281	49±53	6.3±4.7
1-NP	1245±303	536±230	70±53	79±104
2-NFR+2-NP	4974±3219	34975±7905	319±358	281±314
6-NC	4473±715	523±254	23±14	50±39
7-NBaA	605±389	444±142	8.4±6.4	2.1±1.1
6-NBaP	1345±451	174±137	8.4±5.7	4.3±6.1
3-NPer	115±37	62±31	4.3±4.4	2.8±4.4
Total	14063±4836	38912±8524	456±439	379±427

All data represent mean ± S.D.

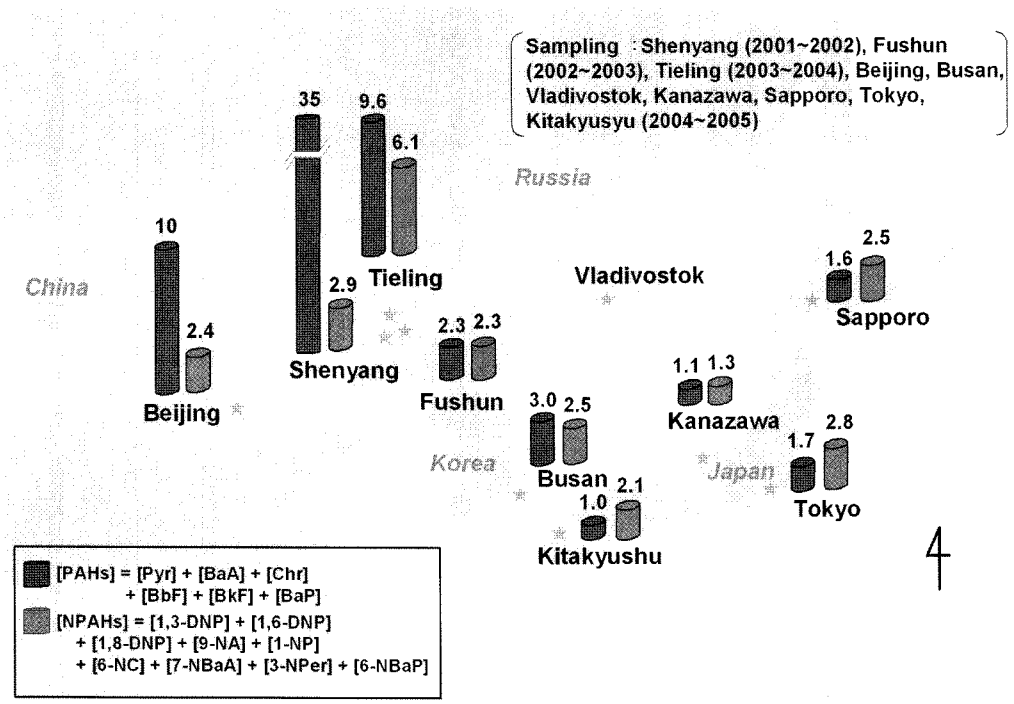

Fig. 2. Winter to summer ratios of the concentrations of PAHs and NPAHs in East Asian cities.

industrial situation of those countries. Among these pollutants, PAHs and NPAHs need to be monitored because of their health risks to humans, as described above and they are present throughout the environment. In East Asian countries, the research on the atmospheric PAHs was widely carried out so far (Chang *et al.*, 2006; Liu *et al.*, 2000). However, only a few studies have been reported concerning the emission and behavior of atmospheric NPAHs, because the concentrations of them are significantly lower than those of PAHs. In our previous studies, we developed a highly sensitive and selective detection method for NPAHs, and improved it for the practical use (Tang *et al.*, 2005, 2003; Hayakawa *et al.*, 2001; Murahashi and Hayakawa, 1997; Hayakawa *et al.*, 1991). Utilizing this method, we studied the characteristics and major contributors of atmospheric PAHs and NPAHs in cities in Japan, Korea, China and Russia. The purpose of this report is to review recent results obtained from the international collaboration researches.

2. CONCENTRATIONS OF ATMOSPHERIC PAHs AND NPAHs

We collected airborne particulates in ten cities in the above four countries, Beijing, Shenyang, Fushun and Tieling (China), Vladivostok (Russia), Busan (South Korea), Kitakyushu, Kanazawa, Tokyo and Sapporo (Japan), in winter and summer from 1997 to 2005 (Tang *et al.*, 2005, 2002a, b; Kakimoto *et al.*, 2002, 2001). Six PAHs and eleven NPAHs in the extracts from the particulates were analysed by HPLC with fluorescence and chemiluminescence detections, respectively. The PAHs were pyrene (Pyr), benz[*a*] anthracene (BaA), chrysene (Chr), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF) and BaP, and NPAHs were 1, 3-, 1, 6-, 1, 8-DNPs, 1, 2-NPs, 2-NFR, 9-nitroanthracene (9-NA), 6-NC, 7-nitrobenz[*a*] anthracene (7-NBaA), 3-nitropelyrene (3-NPer) and 6-nitrobenzo[*a*]pyrene (6-NBaP).

The total PAH concentrations were in the order: Fushun > Shenyang ≃ Tieling > Beijing > Vladivostok > Kitakyushu > Sapporo > Busan > Tokyo > Kanazawa. The total NPAH concentrations were in the order: Fushun > Beijing > Tieling > Shenyang > Tokyo > Vladivostok ≃ Kitakyushu > Sapporo > Kanazawa (Fig. 1). Thus, the concentrations of the four Chinese cities were much higher than those of the cities in the other countries. As a sample, Table 1 shows the atmospheric concentrations of PAHs and NPAHs in winter and summer in Fushun and Kanazawa, respectively. The atmospheric concentrations of PAHs and NPAHs were about 360 and 54 times higher than in Kanazawa in winter, respectively. In summer, the atmospher-

Table 2. Factor analysis with varimax rotation of PAHs and NPAHs in three clusters grouped by cluster analysis.

Compounds	Clustor 1			Clustro 2			Clustor 3		
	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 3
Flu	**0.95**	0.20	0.14	**0.98**	0.02	0.16	**0.85**	0.40	0.16
Pyr	**0.96**	0.20	0.14	**0.98**	0.15	0.08	**0.99**	0.20	0.08
BaA	**0.96**	0.21	0.19	**0.98**	0.00	0.10	**0.77**	0.53	0.26
Chr	**0.96**	0.21	0.17	**0.95**	0.00	0.30	**0.86**	0.44	0.23
BbF	**0.93**	0.28	0.24	**0.86**	−0.13	0.50	**0.93**	0.22	0.24
BkF	**0.93**	0.27	0.24	**0.89**	−0.15	0.43	**0.85**	0.41	0.24
BaP	**0.93**	0.26	0.24	**0.94**	−0.03	0.32	**0.94**	0.25	0.23
BgPe	**0.78**	0.32	0.37	**0.78**	−0.28	0.47	**0.92**	0.26	0.27
IDP	**0.89**	0.28	0.29	**0.87**	−0.15	0.45	**0.91**	0.35	0.21
1,3-DNP	0.43	**0.77**	0.10	0.53	**0.77**	−0.01	**0.92**	0.21	0.23
1,6-DNP	0.41	0.53	0.40	0.22	**1.00**	0.04	**0.75**	0.38	0.38
1,8-DNP	0.29	0.28	**0.92**	−0.10	**0.98**	−0.09	**0.78**	0.39	0.36
1-NP	0.07	**0.87**	0.18	−0.17	**0.87**	−0.06	**0.84**	0.28	0.32
Eigenvalue	8.10	2.27	1.56	7.94	2.88	1.70	7.30	3.40	1.40
Variance (%)	62.28	17.49	11.96	61.05	22.18	13.08	56.46	25.88	10.74
Cumulative (%)	62.28	79.77	91.74	61.05	83.24	96.32	56.46	82.35	93.08

Only factor loadings > 0.7 are in bold.

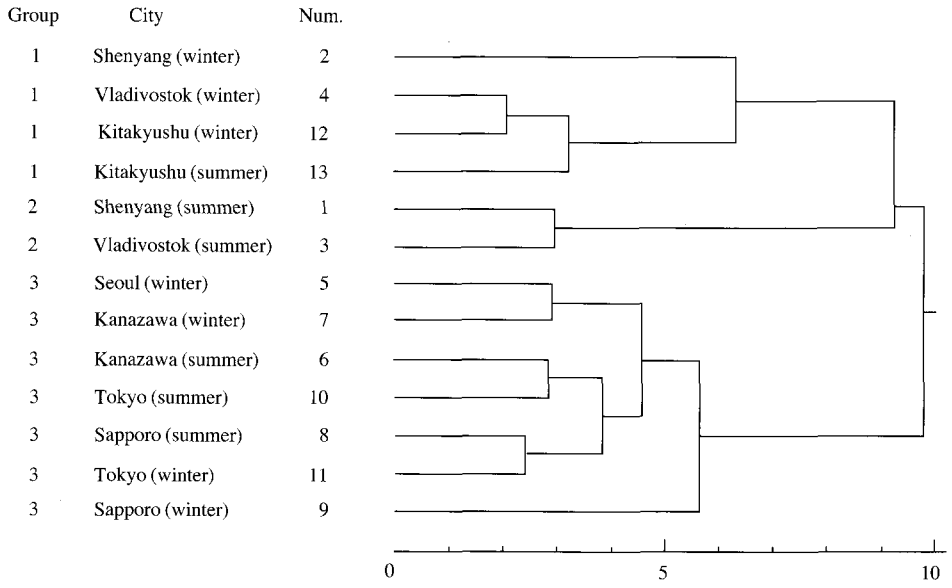

Fig. 3. Cluster analysis dendrogram of atmospheric PAHs and NPAHs in East Asian cities by using Ward's method and standardized squared Euclidean distance.

ic concentrations of the atmospheric concentrations of NPAHs also were about 170 and 26 times higher than in Kanazawa, respectively. On the other hand, the winter to summer ratios of the concentrations of PAHs and NPAHs were higher than 1 in all cities (Fig. 2). Among the cities, the winter to summer ratios of PAHs were the highest in Chinese cities. However, the winter to summer ratios of NPAHs were not as high as the winter to summer ratios of PAHs (Fig. 2). A possible cause of the large seasonal variation observed in Chinese cities is the emission of a large amount of particulates, which contain high concentrations of PAHs but not high concentrations of NPAHs, in winter.

In order to clarify the difference of distribution of individual PAHs and NPAHs in atmosphere in East Asian cities, cluster analysis and factor analysis were used (Tang *et al.*, 2005). For the cluster analysis, the concentrations of individual PAHs and NPAHs were expressed as percentages of the total PAH and NPAH concentrations, respectively. As shown in Fig. 3, the cities formed three large clusters. Cluster 1 includes Shenyang (winter), Vladivostok (winter), Kitakyushu (winter) and Kitakyushu (summer). Cluster 2 includes

Shenyang (summer) and Vladivostok (summer). Cluster 3 includes Seoul (winter), Kanazawa (winter), Kanazawa (summer), Tokyo (summer), Tokyo (winter), Sapporo (summer) and Sapporo (winter). The principal factors were extracted from each cluster by the factor analysis method. The factor analysis used all data of the atmospheric concentrations of the nine PAHs and four NPAHs at monitoring stations in the same cluster. Three factors which account for over 90% of the total variance were identified in each cluster (Table 2). In cluster 1, the first factor (explaining 62.3% of the variance) made a large contribution. High factor loadings (>0.7) of all PAHs and lower factor loadings of all NPAHs were obtained in this factor. This result suggests that the main contributor contained high concentrations of PAHs but not NPAHs in Shenyang (winter), Vladivostok (winter), Kitakyushu (summer) and Kitakyushu (winter). In cluster 2, factor 1 explained 61.1% of the variance and included all PAHs. Factor 2 explained 22.2% of the variance and included all NPAHs. This suggests that multiple sources might contribute to the atmospheric PAHs and NPAHs in summer in Shenyang and Vladivostok. In cluster 3, higher factor loading (>0.7) of all PAHs and NPAHs were obtained in factor 1 (which explained 56.5% of the variance). It is likely that all these compounds originated from the same types of sources in Seoul (winter), Kanazawa (winter), Kanazawa (summer), Tokyo (summer), Tokyo (winter), Sapporo (summer) and Sapporo (winter).

3. MAJOR CONTRIBUTORS OF ATMOSPHERIC PAHs AND NPAHs

Fuels such as oil, coal and firewood are the main emission sources of PAHs and NPAHs. Moreover, most of these are bound to particulates suspended in the air. Many studies have shown that motor vehicles (especially diesel-engine vehicles), factories, and home heating are the principal sources of atmospheric PAHs and NPAHs in Asian urban air (Ho and Lee, 2002; Park *et al.*, 2002; Yang *et al.*, 2002; Hayakawa *et al.*, 1995). Concentration ratios of several PAHs such as [BaA]/([Chr]+[BaA]) in the atmosphere have been reported as indicators of their main sources. However, these diagnostic ratios by themselves were not effective enough to identify major sources (Lohmann *et al.*, 2000). As shown in Table 3, the concentration ratios of NPAHs to PAHs were found to be quite different between particulates exhausted from coal stoves and diesel-engine vehicles. The concentration ratio of total NPAHs to total PAHs ([NPAHs]/[PAHs]) was much smaller in coal stove particulates

Table 3. Concentrations of PAHs and NPAHs in particulates exhausted from coal stoves and diesel-engine vehicles.

Compound	Coal stove (n=4)	Diesel-engine vehicle (n=11)
PAH (nmol mg^{-1})		
FR	4.0±1.7	0.18±0.13
Pyr	3.5±1.5	0.18±0.18
BaA	0.9±0.4	0.04±0.03
Chr	0.9±0.8	0.07±0.04
BbF	1.0±0.9	0.03±0.02
BkF	0.2±0.1	0.01±0.01
BaP	0.5±0.3	0.01±0.01
BgPe	0.6±0.3	0.01±0.01
IDP	0.3±0.2	0.01±0.01
Total	12±4.9	0.5±0.35
NPAH (pmol mg^{-1})		
1,3-DNP	0.02±0.03	0.19±0.19
1,6-DNP	0.05±0.08	0.16±0.15
1,8-DNP	0.06±0.05	0.21±0.19
1-NP	1.43±1.28	65.5±55.6
Total	1.56±1.44	66.2±56.1

All data represent mean±S.D.

than that in diesel particulates. Since PAHs are formed at high temperature and throughly they are partly nitrated in the presence of nitrogen oxides, the yield of NPAHs from the corresponding PAHs would increase with increasing in combustion temperature. Therefore, the yield of NPAHs from coal stoves, which burn at about 900-1,000°C, might be smaller than that from diesel-engine vehicles, which run at 2,500-2,700°C. This difference suggests that the ratio of mono-NPAH to its mother PAH is also a useful indicator for contributions at different temperatures (Tang *et al.*, 2005). From above considerations, we selected the [1-NP]/[Pyr] ratio as the new indicator of the contribution of diesel-engine vehicles and coal combustion to atmospheric PAHs and NPAHs in the East Asian cities. The value of airborne particulates was in the range from 0.002 (Tieling) to 0.005 (Beijing) in the four Chinese cities in winter. This smaller ratio appeared to be similar to that of coal stove particulates (0.0004) and other coal combustion systems such as coal heaters in China. On the other hand, the ratios of Korean and Japanese cities were in the range from 0.031 (Busan) to 0.095 (Kanazawa) in winter. These larger ratios suggested that the contribution of diesel-engine exhaust particulates (0.36) might be large (Tang *et al.*, 2005).

4. SECONDARY FORMATION OF NPAHs

PAHs are emitted from primary sources in the

atmosphere. However, some NPAHs such as 2-NP and 2-NFR are aso produced from the parent PAH by the gas phase reactions with hydroxyl radicals during the daytime, and with nitrate radicals at nighttime in the presence of oxides of nitrogen in the atmosphere (Arey *et al.*, 1986; Pitts *et al.*, 1985). In order to determine how these NPAHs are formed in the atmosphere, the diurnal concentrations of 2-NFR, 2- and 4-NPs and 6-NC were compared with the concentration of 1-NP, which was directly emitted from automobiles, over the same 24 hour period (Fig. 4A, B) (Hayakawa *et al.*, 2000; Murahashi *et al.*, 1999). Both 4-NP and 6-NC showed their maximum concentrations at 12:00, which was the same time when 1-NP showed its maximum concentration (Fig. 2A). This result suggested that the atmospheric behaviors of 4-NP and 6-NC were similar to the atmospheric behavior of 1-NP. However, the concentrations of 2-NFR and 2-NP (Fig. 2B) increased in the daytime and reached their maximum concentrations at 18:00, which was six hours later than the time of the maximum concentration of 1-NP. The diurnal patterns of the FR and Py concentrations were similar to the pattern of 1-NP and the concentration of OH radicals also might increase in the daytime. Under these conditions, the increases of the concentrations of 2-NFR and 2-NP in the daytime suggested that the two compounds were mainly formed by OH radical-initiated reaction according to the above mechanisms.

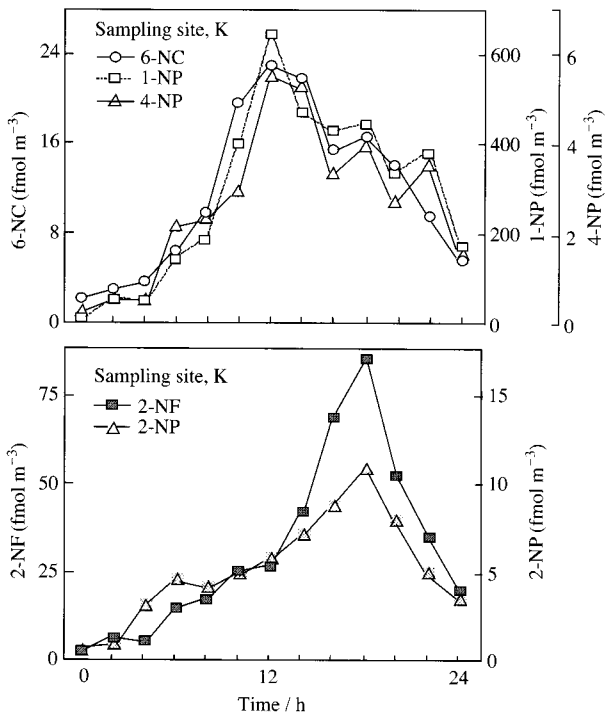

Fig. 4. Diurnal concentrations of 6-NC, 1- and 4-NPs (A) and 2-NFR and 2-NP (B) in the atmosphere at Kanazawa, Japan on January 6, 1995. Horizontal bars indicate mean values.

On the other hand, the concentration of 2-nitrobenzanthrone (2-NBA, 1.83 pmol/m^3) in airborne particulates collected at a heavy traffic road site in Kanazawa, Japan was about two orders of magnitude higher than the concentration of 3-NBA (0.025 pmol/m^3) in the same sample. However, based on localization energies, the direct nitration of the carbon positions in benzanthrone was found to be in the order: $3>4>1>9\simeq11>6>5\simeq2>8\simeq10$ (Hida, 1967). The concentration order appears to be inconsistent with this order. This is because most atmospheric 2-NBA might be formed in the atmosphere rather than in

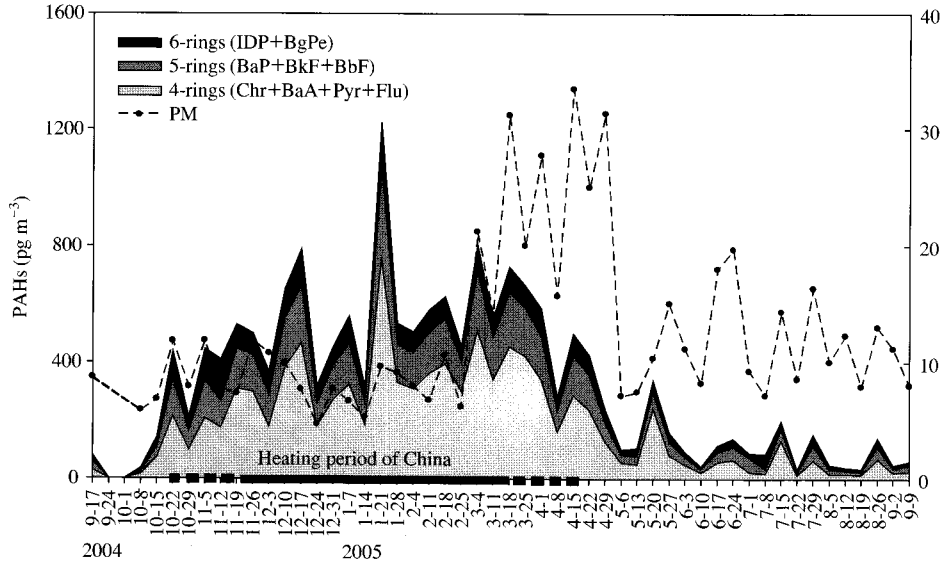

Fig. 5. Weekly variations of PAHs and PM at Wajima during the sampling period. Dates indicate the first day of a 7 day sampling period.

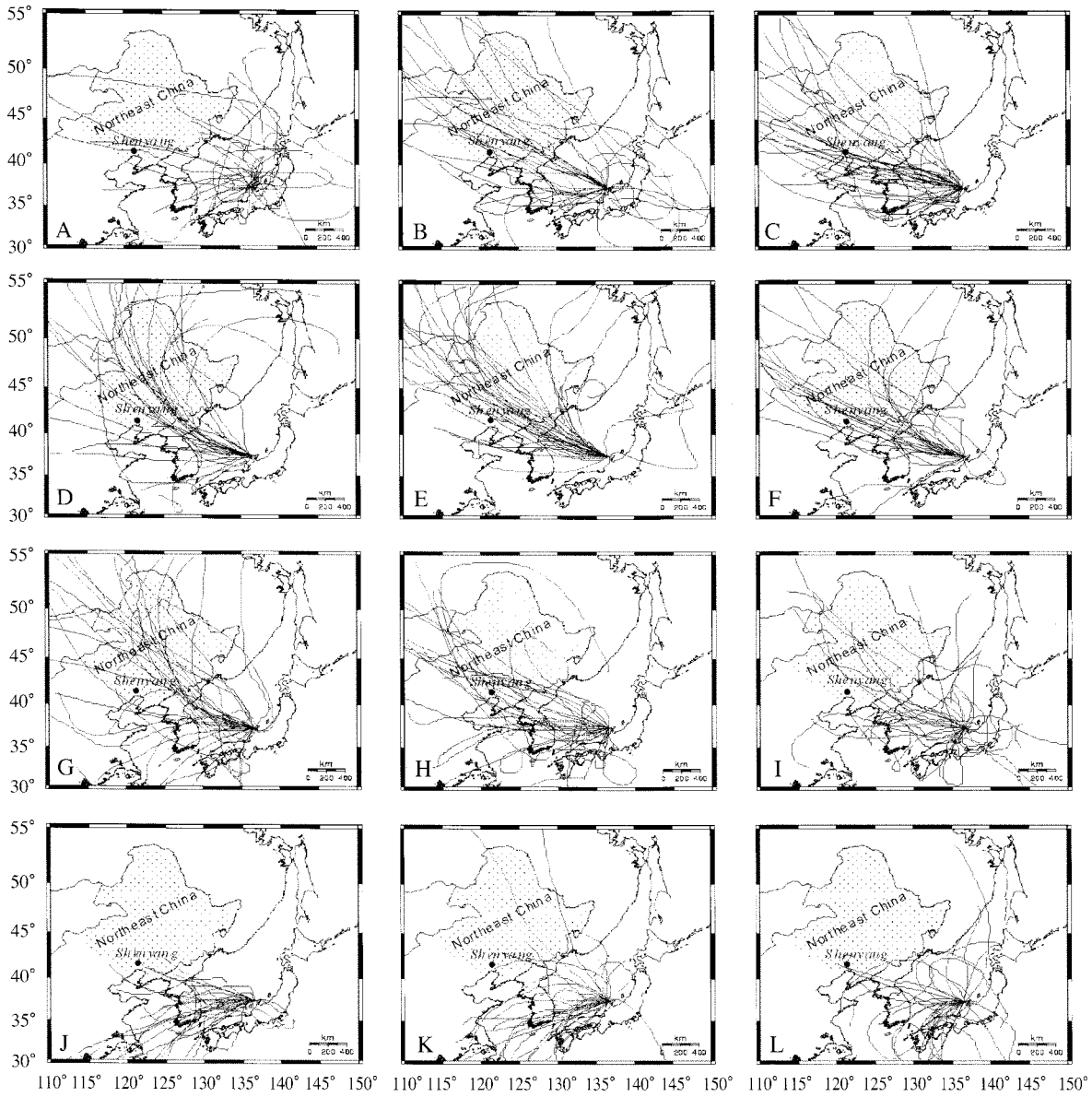

Fig. 6. Back trajectory analysis of air samples. (A) 15, Sep. 2004-14, Oct. 2004; (B) 15, Oct. 2004-14, Nov. 2004; (C) 15, Nov. 2004-14, Dec. 2004; (D) 15, Dec. 2004-14, Jan. 2005; (E) 15, Jan. 2005-14, Feb. 2005; (F) 15, Feb. 2005-14, Mar. 2005; (G) 15, Mar. 2005-15, Apr. 2005; (H) 16, Apr. 2005-14, May 2005; (I) 15, May 2005-14, Jun. 2005; (J) 15, Jun. 2005-14, Jul. 2005; (K) 15, Jul. 2005-14, Aug. 2005; (L) 15, Aug. 2005-14, Sep. 2005.

burning processes, such as that in a diesel-engine (Tang *et al.*, 2004). This result suggested that several NPAHs are not only originated from primary sources but also produced in the atmosphere.

5. LONG RANGE TRANSPORT OF PAHs

Not only sulfur dioxide but also Asian dust is transported from the Asian Continent to Japan in the winter and spring seasons (Uno *et al.*, 1997; Iwasaka *et al.*, 1983). These facts suggest that other pollutants such as PAHs also might be transported to Japan, which is in the path of winds from the Asian Continent. We collected airborne particulates at Wajima, on the Noto Penissula, Ishikawa, Japan by a high-volume air sampler with a quartz filter every day from 17 September 2004 to 16 September 2005. There were no major contributors of PAHs and NPAHs such

as heavy traffic roads or factories near this sampling site (Yang *et al.*, 2007). As shown in Fig. 5, higher atmospheric PAHs concentrations were observed at Wajima during the heating period of China. A principal component analysis showed that the composition of nine PAHs at Wajima, during the heating period of China, was close to that at Shenyang (China) but not to that of Kanazawa (Japan), although the concentrations of nine PAHs in Wajima were about 400 times lower than in Shenyang (Yang *et al.*, 2007). Meteorological analysis indicated that the air was transported from Northeast China over the Japan Sea in the above period (Fig. 6). These results strongly suggest that PAHs emitted in China, during the heating period, were transported over long distances to Japan.

However, we have not found any correlation between the Asian dust events and the atmospheric PAHs at Wajima from above result (Sun, 2002). This might be because the Asian dust produced in clean areas and entrained at high elevations ($>5{,}000$ m) collected at Wajima during our research period. The same result was observed in our other study (Tamamura, 2007).

6. CONCLUSION

As conclusions, the atmospheric concentrations of PAHs and NPAHs were much higher in Chinese cities than in Korean and Japanese cities. The main contributors were coal combustion systems such as coal-heating systems in winter in China while automobiles in Korea and Japan. The high level PAHs detected at Wajima were the result of long-range transport from China. However, the mechanism of chemical reaction, such as nitration reaction of PAHs, during the transportation from Asian continent to Japan is not clarified. This might become one of our next subjects.

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