Genes and Environment, Vol. 36, No. 3 pp. 152–159 (2014)

Review

Atmospheric Behaviors of Polycyclic Aromatic Hydrocarbons in East Asia

Kazuichi Hayakawa[1,2,4], Ning Tang[1], Takayuki Kameda[3] and Akira Toriba[1]

[1]Faculty of Pharmaceutical Science, Institute of Medical, Pharmaceutical and Health Sciences, Kanazawa University, Kanazawa, Japan
[2]Institute of Nature and Environmental Technology, Kanazawa University, Kanazawa, Japan
[3]Graduate School of Energy Science, Kyoto University, Kyoto, Japan

Received April 28, 2014; Revised May 28, 2014; Accepted May 29, 2014
J-STAGE Advance published date: June 7, 2014

Airborne particulates have been continuously collected at four cities in Japan starting in the late 1990s, at major cities in China, Korea and Russia starting in 2001 and at Noto peninsula starting in 2004. After extracting and cleaning up particulates, nine polycyclic aromatic hydrocarbons (PAHs) and eleven nitropolycyclic aromatic hydrocarbons (NPAHs) were determined by HPLC with fluorescence and chemiluminescence detections, respectively. Annual concentrations of PAHs and NPAHs at the cities were in the order, China > Russia > Korea > Japan. Concentrations of PAHs and NPAHs in Japanese cities significantly decreased but different tendencies were observed in Chinese and Russian cities. On the Noto peninsula, which is in the main path of winter northwest winds and a year-round jet stream that blow from the Asian continent to Japan, the concentrations of PAHs and NPAHs were high in winter and low in summer every year. A cluster analysis and back trajectory analysis indicated that PAHs and NPAHs at the Noto peninsula in winter mainly came from coal burning systems in Northeast China.

Key words: polycyclic aromatic hydrocarbon, nitropolycyclic aromatic hydrocarbon, $PM_{2.5}$, East Asia, long-range transport

Introduction

In East Asia, the economics and industrial outputs of Japan, China, Korea and Russia have developed rapidly in recent decades. Together, these countries account for more than a quarter of the world energy consumption. The main energy sources in these countries are oil in Japan and Korea, coal in China and natural gas in Russia (but coal for Far Eastern Russia). The burning of these fuels releases many pollutants including gases and particulates into the atmosphere. Recent increases in the consumption of coal and petroleum in China have led to heavy air pollution. One class of small atmospheric pollutants is refereed to as ''atmospheric particulate matters not more than 2.5 μm ($PM_{2.5}$)''. High levels of $PM_{2.5}$ have been reported in Beijing since January 2013 (1).

Polycyclic aromatic hydrocarbons (PAHs) such as benzo[*a*]pyrene (BaP) and nitropolycyclic aromatic hydrocarbons (NPAHs) such as 1-nitropyrene (1-NP) are ubiquitous environmental pollutants, which mainly originate from imperfect combustion and pyrolysis of organic matters (2). In addition, some NPAHs, such as 2-NP and 2-nitrofluoranthene (2-NFR), are secondarily formed in the atmosphere via reactions of their parent PAHs and NO_2 (3). Many of them are carcinogenic and/or mutagenic. The International Agency for Research on Cancer ranked BaP in Group 1 (carcinogenic to humans), 1-NP in Group 2A (probably carcinogenic to humans) and several other PAHs and NPAHs in Group 2B (possibly carcinogenic to humans). Additionally, WHO moved $PM_{2.5}$ in Group 1 in 2013, because several PAHs and NPAHs, such as BaP and 1-NP, contained in $PM_{2.5}$ are in Group 1 or Group 2A (4). On the other hand, several metabolites of PAHs and NPAHs have estrogenic/antiestrogenic or antiandrogenic activities (5–7) or activity to produce reactive oxygen species (8,9). Because PAHs and NPAHs have been linked to respiratory and cardiovascular diseases, the environmental behaviors need to be better understood.

Airborne particulates were collected at four major cities (Kanazawa, Tokyo, Sapporo and Kitakyushu) in Japan from the late 1990s. The sampling area was expanded to major foreign cities in Pan-Japan Sea countries, Shenyang, Tieling, Fushun and Beijing (China), Busan (Korea) and Vladivostok (Russia) starting in 2001. The international collaboration in airborne particulate sampling has continued to the present with the

[4]Correspondence to: Faculty of Pharmaceutical Science, Institute of Medical, Pharmaceutical and Health Sciences, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan. Tel: +81-76-234-4413, Fax: +81-76-234-4456, E-mail: hayakawa@p.kanazawa-u.ac.jp
doi: org/10.3123/jemsge.2014.016

addition of several cities such as Shanghai in China.

Airborne particulates were extracted with benzene/ethanol and the extracts were cleaned up with alkaline solution, acidic solutions and water. Then PAHs and NPAHs were determined. The United States EPA has listed 16 PAHs as priority pollutants. In this study we measured nine of these PAHs having 4 to 6 rings, by HPLC with fluorescence detection using pyrene-d_{10} (Pyr-d_{10}) and benzo[*a*]pyrene-d_{12} (BaP-d_{12}) as internal standards (10,11). The nine PAHs were fluoranthene (FR), pyrene (Pyr), benz[*a*]anthracene (BaA), chrysene (Chr), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), BaP, benzo[*ghi*]perylene (BghiPe) and indeno[1,2,3-*cd*]pyrene (IDP).

Using the same extracts that were used for the PAH analysis, were measured eleven NPAHs by HPLC with chemiluminescence detection using 2-fluoro-7-nitrofluorene (FNF) as an internal standard (12–14). The eleven NPAHs were 1,3-, 1,6-, 1,8-dinitropyrenes (1,3-, 1,6-, 1,8-DNPs), 9-nitroanthracene (9-NA), 1-, 2-NPs, 2-nitrofluoranthene (2-NFR), 6-nitrochrysene (6-NC), 7-nitrobenz[*a*]anthracene (7-NBaA), 6-nitrobenzo[*a*]pyrene (6-NBaP) and 3-nitroperylene (3-NPer). The system time-programed the following five steps: 1) separation of NPAHs from PAHs in a clean-up column, 2) reduction of NPAHs to their corresponding amino derivatives (APAHs) in a reduction column packed with Pt/Rh, 3) concentration of APAHs on a concentrator column, 4) separation of APAHs in a separation column and 5) detection of APAHs chemilumigenically. The sensitivity of the HPLC with chemiluminescence detection was about 100 times higher than the sensitivities of previous methods such as HPLC with fluorescence detection and GC-MS (12).

Atmospheric Concentrations of PAHs and NPAHs

Figure 1 shows the annual mean atmospheric concentrations of total PAHs and NPAHs at the above cities from 2001 to 2005 (10,11,15–20). The PAH concentrations were in the order; Fushun > Beijing > Tieling > Shenyang ≫ Vladivostok > Tokyo > Sapporo > Kitakyushu > Busan > Kanazawa. The NPAH concentrations were in the order; Fushun > Beijing > Tieling > Shenyang > Tokyo > Vladivostok = Kitakyushu > Busan > Sapporo > Kanazawa. Although there were small differences in the order of cities, the PAH and NPAH concentrations in the four countries were in the

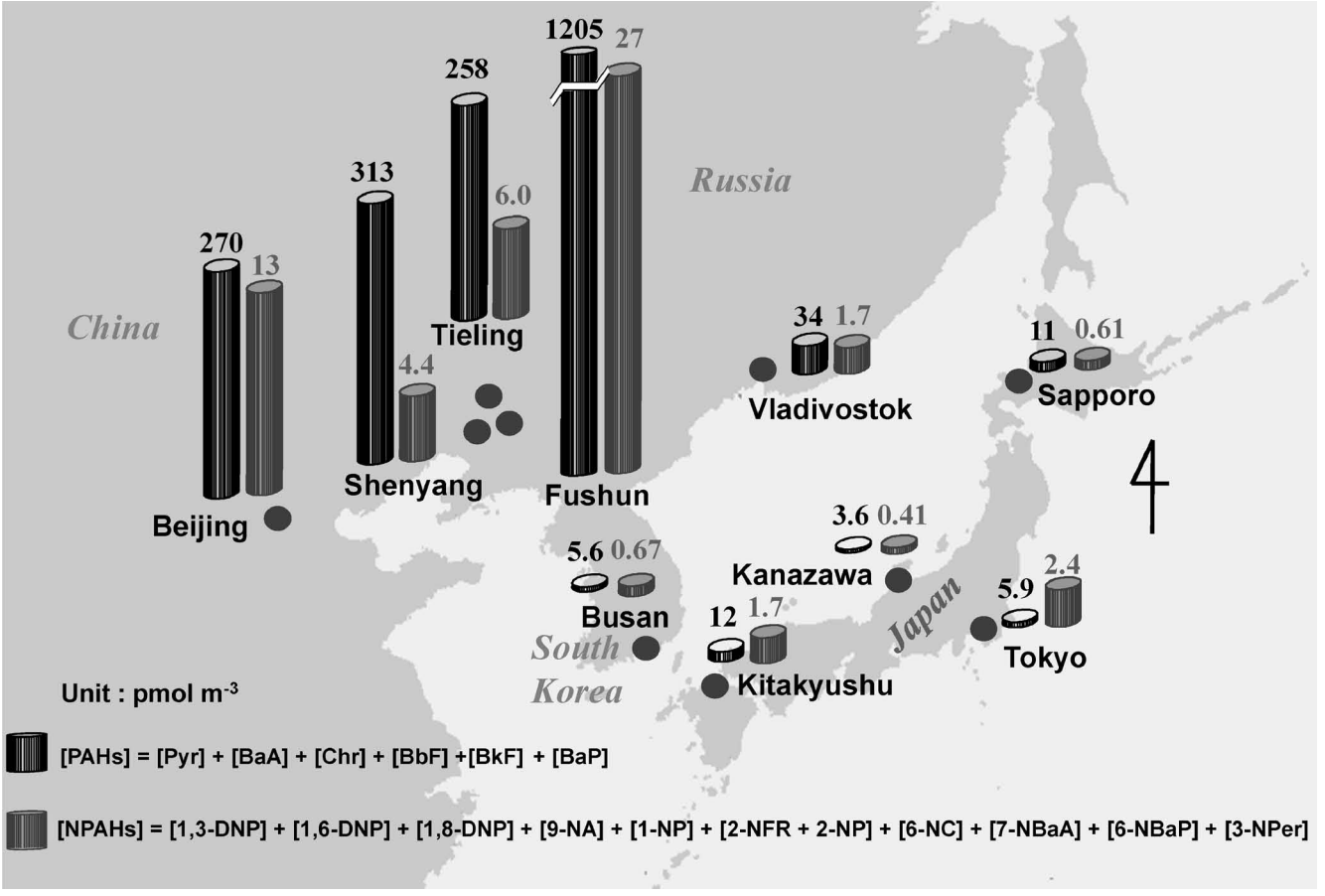


Fig. 1. Annual average atmospheric concentrations of PAHs and NPAHs in East Asia.

order, China > Russia > Korea = Japan. It must be emphasized that the PAH concentrations in China were much higher than those in Japan, suggesting that the urban atmosphere in China was very much polluted with PM-containing PAHs. Moreover, Fig. 1 showed that the concentration ratios of NPAHs to PAHs ([NPAHs]/[PAHs]) were smaller at Chinese cities (0.014–0.048) than those at Japanese cities (0.055–0.407), suggesting that the sources were different between the two counties (11).

Compositions and Main Sources

The formation of NOx depends on the combustion temperature and the formation of NPAHs from corresponding PAHs in the presence of NOx also depends on combustion temperature of organic matters. Therefore, the formation of NPAHs increased with increasing combustion temperature, suggesting that the [NPAH]/[PAH] concentration ratios in PM might also depend on combustion temperature. To test this hypothesis, the [NPAH]/[PAH] concentration ratios were determined in three different types of PM from diesel-engine vehicles (combustion temperature was about 2,700°C), coal-burning stoves (about 900°C), and wood burning stoves (about 500°C). Four of the ratios ([1-NP]/[Pyr], [6-NC]/[Chr], [7-NBaA]/[BaA] and [6-NBaP]/[BaP]) were significantly different in the three PMs (Fig. 2), suggesting that these parameters showed the sources clearly (11,21). A high concentration of 1-NP in the PM in automobile exhausts has been used as an effective marker of human exposure to automobile exhausts (22–25).

Figure 2 showed very different values of [1-NP]/[Pyr], [6-NC]/[Chr], [7-NBaA]/[BaA] and [6-NBaP]/[BaP] in diesel-engine particulates (DEP), coal-smoke particulates (CSP) and wood-smoke particulates (WSD). The figure, for example, showed the [1-NP]/[Pyr] ratio of CSP (0.001) was much smaller than the ratio of DEP (0.36) (11). In East Asian cities, DEP and/or CSP were considered as major contributors. The [1-NP]/[Pyr] ratios at Shenyang were 0.003 (winter) and 0.04 (summer), while the values at Tokyo were 0.13 (winter) and 0.09 (summer), respectively. The difference in the values between the two cities in winter (more than 40 times) was larger, probably because of a larger amount of emissions from coal heating in Shenyang. Several PAH pairs such as [FR]/[FR + Pyr], [BaA]/[Chr] and [IDP]/[IDP + BghiPe] have been used as markers of the source of the PAHs (2,26,27). However, the differences in those markers were not large enough to identify the source. Thus, by using the [NPAH]/[PAH] ratios, the major sources of PAHs and NPAHs of the four countries in Fig. 1 were identified as automobiles in Japan and Korea, coal combustion systems in China and Russia (19,28). The values for China were typical of a country that exhausts huge amounts of PAHs and NPAHs from coal combustion systems.

Figure 3 shows diurnal atmospheric concentrations of 1-NP and 1,3-, 1,6-, 1,8-DNPs emitted from automobiles. Airborne particulates were collected every 2 h at

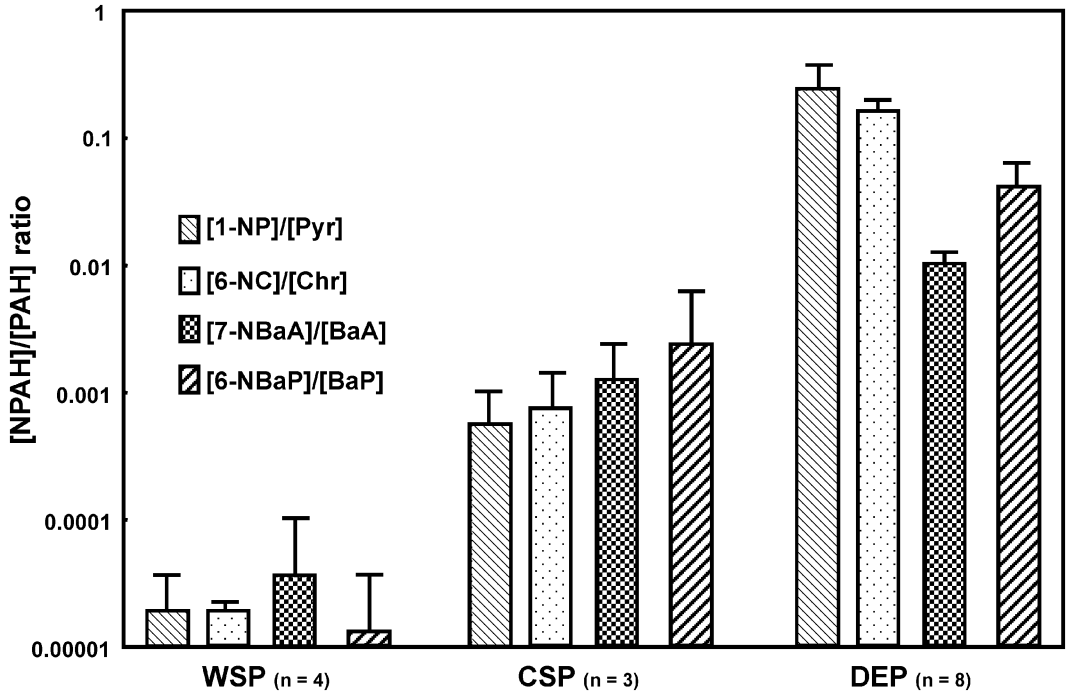


Fig. 2. [NPAH]/[PAH] ratios of diesel-engine exhaust particulates (DEP), coal-smoke particulates (CSP) and wood-smoke particulates (WSP).

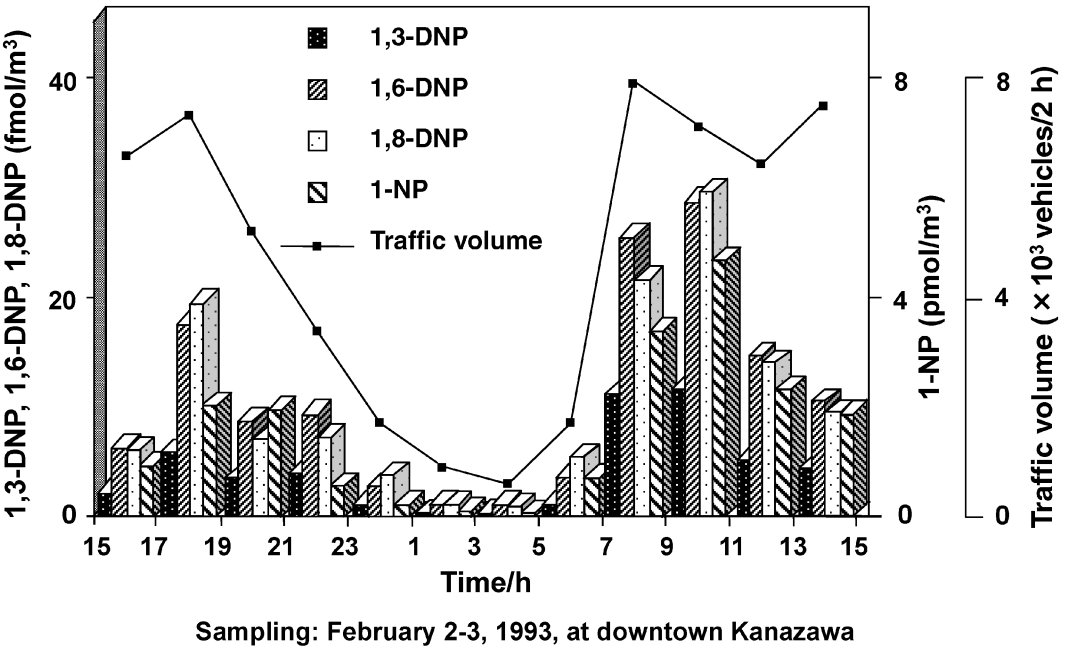


Fig. 3. Diurnal variations of 1,3-, 1,6-, 1,8-DNPs and 1-NP in urban air.

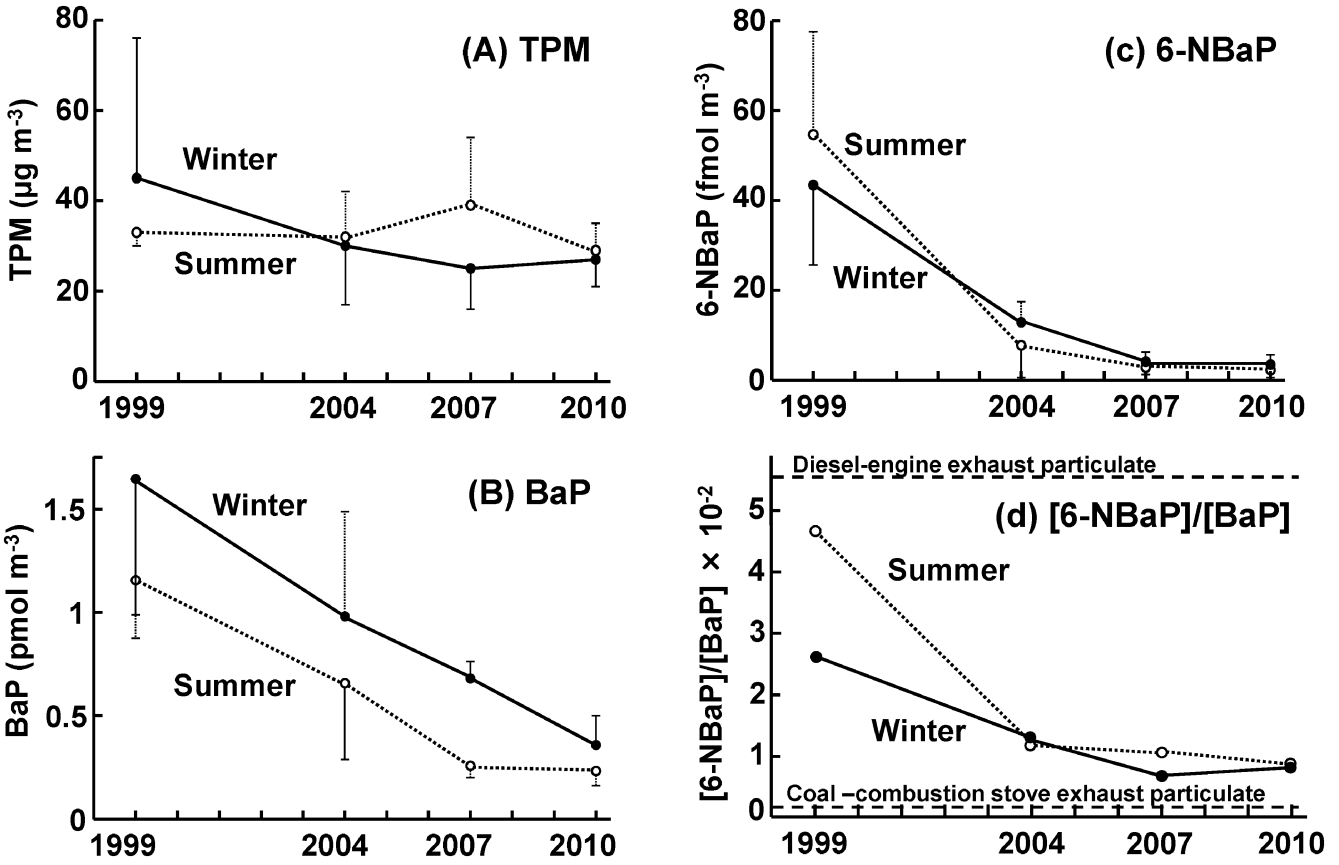
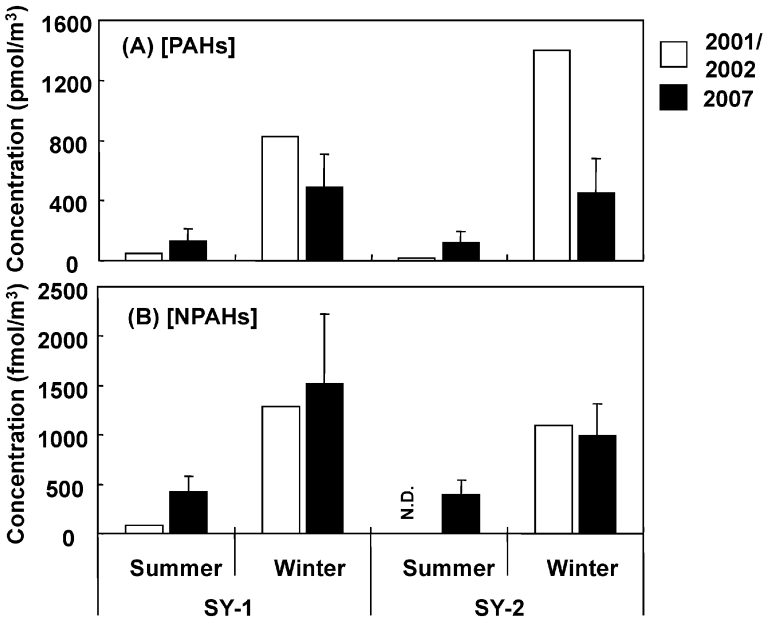


Fig. 4. Changes of atmospheric (A) total particulate matter (TPM), (B) BaP and (c) 6-NBaP concentrations and (d) [6-NBaP]/[BaP] Ratio at downtown Kanazawa.

roadside in downtown Kanazawa city, Japan. Although the concentrations of 1,3-, 1,6- and 1,8-DNPs were much lower than the concentration of 1-NP, the three NPAHs showed very similar patterns. The concentrations of these three NPAHs were high in the evening, decreased in the night and reached in the lowest levels in the early morning. Then they increased later in the morning. The pattern of these NPAHs was in parallel with the time course of traffic volume monitored at the nearest intersection, suggesting that these NPAHs were emitted from automobiles (29). PAHs such as BaP and Pyr showed patterns similar to those of NPAHs. Figure 3 is a typical pattern observed in the downtown area of Japanese cities where the major contributors of PAHs and NPAHs were automobiles (30,31). Both PAHs and NPAHs emitted from automobiles mainly existed in the fine particulate fraction less than 1.1 μm (32,33).

In 1990s, the atmospheric concentrations of PM, which contained PAHs and NPAHs, in Japanese cities were very high and were considered as a cause of respiratory and/or cardiovascular diseases. In the early 2000s, the Japanese government took countermeasures to reduce the urban air pollutions by requiring emission control of PM and NOx from automobiles and diesel/gasoline quality control (34). Some of the results of these measures are shown in Fig. 4. In downtown Kanazawa, total particulate matters (TPM) tended to decrease during the period from 1999 to 2010 (Fig. 4A). Moreover, the concentrations of BaP (Fig. 4B) and 6-NBaP (Fig. 4C) clearly decreased in this period. Especially, the 6-NBaP concentration decreased significantly by a factor of 30 in summer and decreased by a factor of 13 in winter. Moreover, the [6-NBaP]/[BaP] ratio, which is an effective marker of automobile emission, decreased significantly in the same period (Fig. 4D). This suggests that the contribution of automobiles to atmospheric PAHs and NPAHs were effectively reduced by the countermeasures. During this period, the significant decreases of PAHs and NPAHs were also observed in the other Japanese cities (34,35).

In China, local governments started several projects to reduce air pollution. However, the effects were not the same as those in Japan. The Shenyang government undertook the Blue Sky Project (36), in which 100 factories were transferred to the outer city, and 5,000 inefficient boilers for domestic heating were removed between 2001 and 2007. The project helped to reduce the atmospheric concentrations of PM_{10}. As shown in Fig. 5, the project also decreased the concentrations of PAHs in Shenyang (37). The Beijing government started to control traffic volume to reduce air pollution for the 2008 Olympic Games. It is important to know the tendency of the concentrations of both PAHs and NPAHs after then. Thus atmospheric pollution levels in the Pan-Japan Sea countries changes very fast with different tendencies. The follow-up monitoring of these PAHs and NPAHs in East Asian countries is needed to make accurate prediction.



SY-1 and SY-2 located in commercial area residential area, respectively. [PAHs] = [FR] + [Pyr] + [BaA] + [Chr] + [BbF] + [BkF] + [BaP] + [BghiPe] + [IDP]. [NPAHs] = [1-NP] + [6-NC] + [6-NBaP].

Fig. 5. Comparison of atmospheric PAHs and NPAHs at two sites in Shenyang in 2001–2002 and 2007.

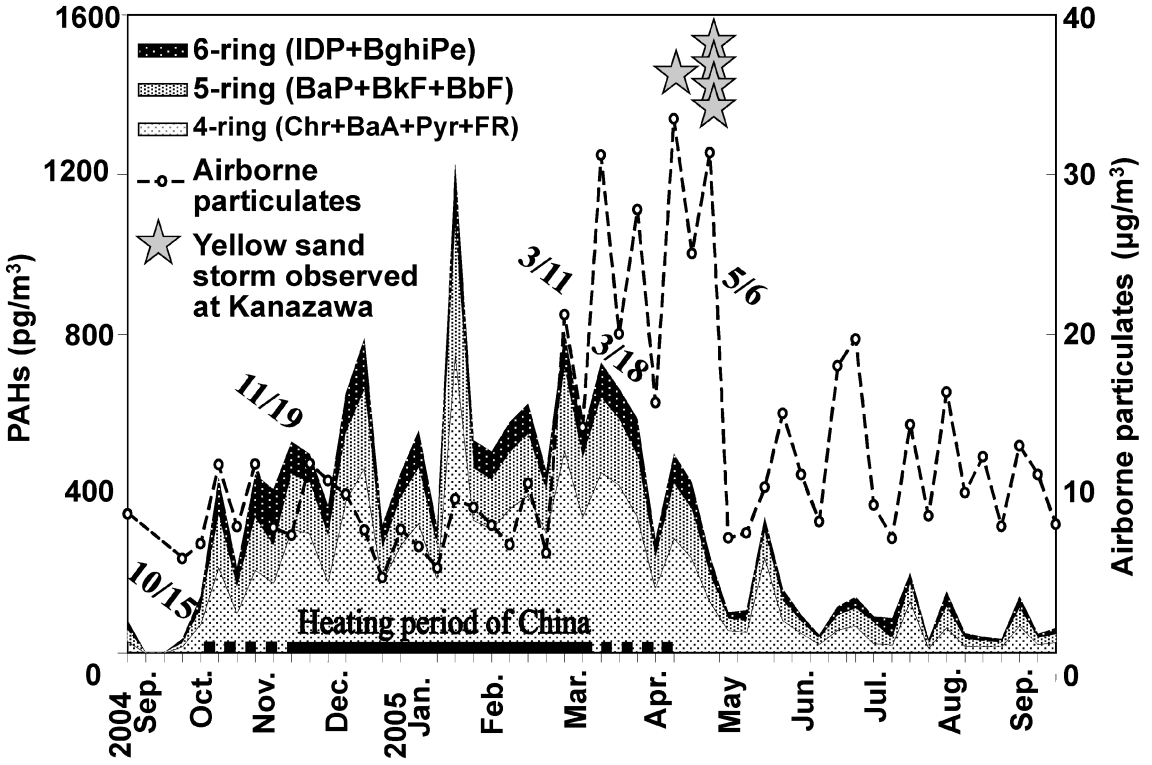


Fig. 6. Time course of atmospheric PAH and particulate concentrations at Noto Peninsula, Japan.

Long-range Transport of PAHs and NPAHs from the Asian Continent to Japan

Airborne particulate matter was collected at the Wajima Air Monitoring Station (Nishi-Futamata-machi, Wajima City, Ishikawa Prefecture, Japan), which is located on the Noto peninsula 2.1 km south of the Japan Sea coast and about 100 km north of Kanazawa. The Noto peninsula is a less-populated area and no major emission sources of atmospheric pollutants are near the station. Airborne particulate matter was collected continuously from September 17, 2004 to the present. This site is in the main path of winter northwest winds and a year-round jet stream that blow from the Asian continent to Japan. The concentrations of PAHs at this site were much higher during the heating period of China (from October 15, 2004 to April 15, 2005) than in other seasons. Airborne particulate concentration, on the other hand, was high from March and May, partly caused by Yellow sand storms. The variation of PAHs was different from that of airborne particulate concentration (Fig. 6) (38). In subsequent years, PAH concentrations repeated the same seasonal variation (high in winter and low in summer).

A cluster analysis dendrogram showed that the chemical composition of atmospheric PAHs at the Noto peninsula was closer to the chemical composition at Shenyang than to the chemical composition at Kanazawa, even though Shenyang is much farther away than Kanazawa. Moreover, a back trajectory analysis showed that the air mass collected at the Noto peninsula in winter passed over Northeast China including Shenyang two or three days before it reached to the Noto peninsula, but it did not pass over this region in other seasons (38). These results indicated that PAHs detected at the Noto peninsula in winter mainly came from Northeast China. The variations in NPAHs were similar to those observed in PAHs, suggesting that the NPAHs have also undergone long-range transport from Northeast China to Japan (39).

During their atmospheric transport, PAHs and NPAHs were converted to other compounds such as their hydroxylated derivatives in the presence of NOx, sunlight or other co-existing compounds such as yellow sand. Some of these compounds were considered to cause respiratory and cardiovascular symptoms (40–45).

Because deterioration of respiratory and cardiovascular symptoms might be caused by yellow sand and $PM_{2.5}$ long-range transported from Asian continent to Japan, as a possible mechanism, continuous monitoring of atmospheric PAHs and NPAHs not only at major cities in Pan-Japan Sea countries but also at Noto peninsula, Japan is very important. By using recent analytical results, the emission sources, concentrations, and transboundary transport of particulate PAHs in Northeast Asia could be estimated accurately (46,47).

Acknowledgements: This research was supported in part by a Grant in Aid for Scientific Research (Nos. 21256001 and 21390034) from the Ministry of Education, Culture, Sports, Science and Technology, Japan, the Environmental Research and Technology Development Funds (Nos. B-0905 and 5-1306) from the Ministry of the Environment, Japan, and Steel Industry Foundation for the Advancement of Environmental Protection Technology.

Conflicts of Interest: The authors declare that there are no conflicts of interest.

References

1 Embassy of The United States, Beijing-China, http://beijing.usembassy-china.org.cn.
2 Rogge WF, Hildemann LM, Mazurek MA, Cass GR, Simoneit BRT. Sources of fine organic aerosol. 2. Noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks. Environ Sci Technol. 1993; 27: 636–51.
3 Arey J, Zielinska B, Atkinson R, Winer AM, Ramdahl T, Pitts JN. The formation of nitro-PAH from the gas-phase reactions of fluoranthene and pyrene with the OH radical in the presence of NOx. Atmos Environ. 1986; 20: 2339–45.
4 IARC, 2014. IARC Monographs on the Evaluation of the Carcinogenic Risks to Humans, Last update: 31 March 2014.
5 Kizu R, Ishii K, Kobayashi J, Hashimoto T, Koh E, Namiki M, et al. Antiandrogenic effect of crude extract of C-heavy oil. Mat Sci Eng C. 2000; 12: 97–102.
6 Hirose T, Morito K, Kizu R, Toriba A, Hayakawa K, Ogawa S, et al. Estrogenic/antiestrogenic activities of benzo[*a*]pyrene monohydroxy derivatives. J Health Sci. 2001; 47: 552–8.
7 Hayakawa K, Onoda Y, Tachikawa C, Hosoi S, Yoshida M, Chung SW, et al. Estrogenic/antiestrogenic activities of polycyclic aromatic hydrocarbons and their monohydroxylated derivatives by yeast two-hybrid assay. J Health Sci. 2007; 53: 562–70.
8 Kumagai Y, Koide S, Taguch K, Endo A, Nakai Y, Yoshikawa T, et al. Oxidation of proximal protein sulfhydryls by phenanthrenequinone, a component of diesel exhaust particles. Chem Res Toxicol. 2000; 15: 483–9.
9 Motoyama Y, Bekki K, Chung SW, Tang N, Kameda T, Toriba A, et al. Oxidative stress more strongly induced by ortho- than para-quinoid polycyclic aromatic hydrocarbons in A549 cells. J Health Sci. 2009; 55: 845–50.
10 Tang N, Oguri M, Watanabe Y, Tabata M, Mishukov VF, Sergienko V, et al. Comparison of atmospheric polycyclic aromatic hydrocarbons in Vladivostok, Toyama and Kanazawa. Bull Jap Sea Res Inst, Kanazawa Univ. 2002; 33: 77–86.
11 Tang N, Hattori T, Taga R, Igarashi K, Yang XY, Tamura K, et al. Polycyclic aromatic hydrocarbons and nitropolycyclic aromatic hydrocarbons in urban air particulates and their relationship to emission sources in the Pan-Japan Sea countries. Atmos Environ. 2005; 39: 5817–26.
12 Hayakawa K, Kitamura R, Butoh M, Imaizumi N, Miyazaki M. Determination of diamino- and aminopyrenes by high performance liquid chromatography with chemiluminescence detection. Anal Sci. 1991; 7: 573–7.
13 Hayakawa K, Noji K, Tang N, Toriba A, Kizu R, Sakai S, et al. A high-performance liquid chromatographic system equipped with on-line reducer, clean-up and concentrator columns for determination of trace levels of nitropolycyclic aromatic hydrocarbons in airborne particulates, Anal. Chim. Acta. 2001; 445: 205–12.
14 Tang N, Toriba A, Kizu R, Hayakawa K. Improvement of an automatic HPLC system for nitropolycyclic aromatic hydrocarbons: Removal of an interfering peak and increase in the number of analytes. Anal Sci. 2003; 19: 249–53.
15 Kakimoto H, Kitamura M, Matsumoto Y, Sakai S, Kanoh F, Murahashi T, et al. Comparison of atmospheric polycyclic aromatic hydrocarbons and nitropolycyclic aromatic hydrocarbons in Kanazawa, Sapporo and Tokyo. J Health Sci. 2000; 46: 5–15.
16 Kakimoto H, Matsumoto Y, Sakai S, Kanoh F, Arashidani K, Tang N, et al. Comparison of atmospheric polycyclic aromatic hydrocarbons and nitropolycyclic aromatic hydrocarbons in an industrialized city (Kitakyushu) and two commercial cities (Sapporo and Tokyo). J Health Sci. 2002; 48: 370–5.
17 Tang N, Tabata M, Mishukov VF, Sergienko V, Toriba A, Kizu R, et al. Comparison of atmospheric nitropolycyclic aromatic hydrocarbons in Vladivostok, Kanazawa and Toyama. J Health Sci. 2002; 48: 30–5.
18 Hayakawa K, Tang N, Kameda T, Toriba A. Atmospheric behaviors of polycyclic aromatic hydrocarbons and nitropolycyclic aromatic hydrocarbons in East Asia. Asian J Atmos Environ. 2007; 1: 19–27.
19 Hattori T, Tang N, Tamura K, Hokota A, Yang XY, Igarashi K, et al. Profiles of particulate-bound polycyclic aromatic hydrocarbons and their nitrated derivatives in three typical cities, Liaoning Province, China. Environ Forensics. 2007; 8: 165–72.
20 Tang N, Araki Y, Tamura K, Dong LJ, Zhang XM, Liu QH, et al. Distribution and source of atmospheric polycyclic aromatic hydrocarbons and nitropolycyclic aromatic hydrocarbons in Tieling city, Liaoning Province, a typical local city in China. Asian J Atmos Environ. 2009; 3: 52–8.
21 Hayakawa K. Review: Study on behaviors and toxities of polycycdlic aromatic hydrocarbons in East Asia. J Jpn Soc Atmos Environ. 2012; 47: 105–10.
22 Miller-Schlze JP, Paulsen M, Toriba A, Hayakawa K, Simpson CD. Analysis of 1-nitropyrene in air particulate matter standard reference materials by using two-dimensional high performance liquid chromatography with online reduction and tandem mass spectrometry detection. J Chromatogr A. 2007; 1167: 154–60.
23 Toriba A, Kitaoka H, Dills R, Mizukami S, Tanabe K, Takeuchi N, et al. Identification and quantification of 1-nitropyrene metabolites in human urine as a proposed

biomarker for exposure to diesel exhaust. Chem Res Toxicol. 2007; 20: 999–1007.
24 Miller-Schlze JP, Toriba A, Tang N, Hayakawa K, Tamura K, Dong L, Simpson CD. Exposures to particulate air pollution and nitro-polycyclic aromatic hydrocarbons amongst taxi drivers in Shenyang, China. Environ Sci Technol. 2010; 44: 216–21.
25 Miller-Schlze JP, Paulsen M, Kameda T, Toriba A, Tnag N, Tamura K, et al. Evaluation of urinary metabolites of 1-nitropyrene as biomarkers for exposure to diesel exhaust in taxi drivers of Shenyang, China. J Expo Sci Environ Epid. 2013; 23: 170–5.
26 Simcik MF, Eisenreich SJ, Lioy PJ. Source apportionment and source/sink relationships of PAHs in the coastal atmosphere of Chicago and Lake Michigan. Atmos Environ. 1999; 33: 5071–9.
27 Khalili NR, Scheff PA, Holsen TM. PAH source fingerprints for coke ovens, diesel and, gasoline engines, highway tunnels, and wood combustion emissions. Atmos Environ. 1995; 29: 533–42.
28 Kong S, Ding X, Bai Z, Han B, Chen L, Shi J, et al. A seasonal study of polycyclic aromatic hydrocarbons in $PM_{2.5}$ and $PM_{2.5\text{-}10}$ in five typical cities of Liaoning Province, China. J Hazard Mater. 2010; 183: 70–80.
29 Hayakawa K, Murahashi T, Butoh M, Miyazaki, M. Determination of 1,3-, 1,6-, and 1,8-dinitropyrenes and 1-nitropyrene in urban air by high-performance liquid chromatography using chemiluminescence detection. Environ Sci Technol. 1995; 29: 928–32.
30 Hayakawa K, Murahashi T, Akutsu K, Kanda T, Tang N, Kakimoto H, et al. Comparison of polycyclic aromatic hydrocarbons and nitropolycyclic aromatic hydrocarbons in airborne and automobile exhaust particulates. Polycycl Aromat Comp. 2000; 20: 179–90.
31 Hayakawa K, Tang N, Akutsu K, Murahashi T, Kakimoto H, Kizu R, et al. Comparison of polycyclic aromatic hydrocarbons and nitropolycyclic aromatic hydrocarbons in airborne particulates collected in downtown and suburban Kanazawa, Japan. Atmos Environ. 2002; 36: 5535–41.
32 Kawanaka Y, Matsumoto E, Sakamoto K, Wang N, Yun SJ. Size distributions of mutagenic compounds and mutagenicity in atmospheric particulate matter collected with a low-pressure cascade impactor. Atmos Environ. 2004; 38: 2125–32.
33 Ho KF, Cao JJ, Lee SC, Chan CK. Source apportionment of $PM_{2.5}$ in urban area of Hong Kong. J Hazard Mater. 2006; 138: 73–85.
34 Hama H, Tokuda T, Izaki A, Ohno T, Watanabe Y, Kanda T, et al. Variation in polycyclic aromatic hydrocarbons and nitropolycyclic aromatic hydrocarbons in airborne particulates collected in urban Kanazawa, Japan in last 12 years. J Jpn Soc Atmos Environ. 2012; 47: 1–8.
35 Hayakawa K. Current topics: Atmospheric pollution and its countermeasure in East Asia from the viewpoint of polycyclic aromatic hydrocarbons. J Health Sci. 2009; 55: 870–8.
36 Shenyang Environmental Protection Bureau of China (http://www.syepb.gov.cn/).
37 Tang N, Tokuda T, Issaki A, Tamura, K, Ji, R, Zhang X, et al. Recent change in atmospheric polycyclic aromatic hydrocarbons and nitropolycyclic aromatic hydrocarbons in Shenyang, China. Environ Forensics. 2011; 12: 342–8.
38 Yang XY, Okada Y, Tang N, Matsunaga S, Tamura K, Kameda T, et al. Long-range transportation of polycyclic aromatic hydrocarbons from China to Japan. Atmos Environ. 2007: 41: 2710–8.
39 Tang N, Sato K, Tokuda T, Yang X, Tatematsu M, Hama H, et al. Factors affecting atmospheric 1, 2-nitropyrenes and 2-nitorfluoranthene in winter at Noto peninsula, a remote gackground site, Japan, Chemosphere. 2014; 107: 324–30.
40 Kameda T, Nakayama Y, Goto T, Koyanagi T, Bandow H, Fujimori K, et al. Photochemical degradation of selected nitro- and oxy-polycyclic aromatic hydrocarbons on airborne particles under simulated solar UV-irradiation. In: Cheng M, Liu W, editors. Airborne Particulates. New York: Nova Science Publishers; 2009. p. 291–307.
41 Kameda T, Akiyama A, Toriba A, Tang N, Hayakawa K. Determination of particle-associated hydroxynitropyrenes with correction for chemical degradation on a quartz fibre filter during high volume air sampling. Int J Environ Anal Chem. 2010; 90: 976–87.
42 Kishida M, Imamura K, Kameda T, Hayakawa K, Bandow H. Determination of oxygenated polycyclic aromatic hydrocarbons in the atmosphere using gas chromatograph-mass spectrometer. J Environ Chem. 2010; 20: 173–81.
43 Kameda T, Akiyama A, Toriba A, Tang N, Hayakawa K. Atmospheric formation of hydroxynitropyrenes from a photochemical reaction of particle-associated 1-nitropyrene. Environ Sci Technol. 2011; 45: 3325–32.
44 Kameda T, Akiyama A, Yoshita M, Tachikawa C, Toriba A, Tang N, et al. Mutagenicities and endocrine-disrupting activities of 1-hydroxy-2-nitropyrene and 1-hydroxy-5-nitropyrene. J Health Sci. 2011; 57: 372–7.
45 Kameda T, Akiyama A, Toriba A, Tang N, Hayakawa K. Atmospheric formation of hydroxynitrofluoranthene from photochemical reactions of 2-nitrofluoranthene. Polycycl Aromat Comp. 2012; 32: 177–87.
46 Inomata Y, Kajino M, Sato K, Ohara T, Kurokawa J, Ueda H, et al. Emission and atmospheric transport of particulate PAHs in Northeast Asia. Environ Sci Technol. 2012; 46: 4941–9.
47 Inomata Y, Kajino M, Sato K, Ohara T, Kurokawa J, Ueda H, et al. Source contribution analysis of surface particulate polycyclic aromatic hydrocarbon concentrations in northeastern Asia by source-receptor relationships. Environ Pollut. 2013; 182: 324–34.