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— Current Topics —

A Problem of Climate Change as Seen by a Pharmaceutical Researcher

Atmospheric Pollution and Its Countermeasure in East Asia from the Viewpoint of Polycyclic Aromatic Hydrocarbons

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The East Asia countries including Japan, China, Korea and Russia have been undergoing a rapid increase of economic and industrial development. However, large amounts of pollutants are released into the air and water. The main energy source, economic stage and lifestale are different in the above four countries and these differences cause the current diverse situation of atmospheric and water pollution in East Asia. This view describes the present stage of atmospheric pollution and countermeasures in East Asia including the author's recent research results concerning polycyclic aromatic hydrocarbons and nitropolycyclic aromatic hydrocarbons.

Key words —— East Asia, atmospheric pollutant, polycyclic aromatic hydrocarbon, nitropolycyclic aromatic hydrocarbon, carbon dioxide

INTRODUCTION

The East Asia countries including Japan, China, Korea and Russia have been undergoing a rapid increase of economic and industrial development. However, large amounts of pollutants are released into the air and water. It has been known that sulfur dioxide emitted from China is transported by the northwest wind in winter season and causes acid rain or acid snow in Japan. Yellow sand (Kosa) is also transported from the Asian continent to Japan in the winter and spring seasons. Recently, a large amount of carbon dioxide emitted from Asia is one of the large issues in the world concerning global warming. The main energy source, economic stage and lifestale are different in the above four countries and these differences cause the current diverse situation of atmospheric and water pollution in East Asia. This view describes the present stage of atmospheric pollution and countermeasures in East Asia including the author's recent research results.

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CHARACTERISTICS OF EAST ASIAN COUNTRIES AND THE CONTRIBUTION TO CARBON DIOXIDE EMISSION

It is well known that the above four countries in East Asia have been developing with large population. The sum of the population of China (1300000000), Russia (140000000), Japan (120000000) and Korea (50000000) is 26.2% of the total population of the world (6200000000). The economical and industrial develop of the above countries have been supported by the large energy consumption. The sum of the energy consumption by Japan, China, Korea and Russia is 25.6% of the total energy consumption in the world (9740000000 ton).

However, the main energy sources are different in the four countries. It has been changed to petroleum from coal in Japan and Korea. The main energy source is still coal (more than 75%) in China (Table 1).[1] The large amount of consumption of fossil fuels exhaust large amount of carbon dioxide. The largest amount of carbon dioxide is emitted from U.S.A. (23.9%). The contribution of China

Table 1. Characteristics of Pan-Japan Sea Countries

Population	
	The sum of the population of China (1300000000), Russia (140000000), Japan (120000000) and Korea (50000000) is 26.2% of the total population of the world (6200000000).
Energy consumption	
	The sum of the energy consumption by Japan, China, Korea and Russia is 25.6% of the total energy consumption in the world (9740000000 ton).
Main energy source	
	Japan, Korea: Oil
	Russia: Natural gas (Far-eastern Russia, Coal)
	China：Coal (68%, the largest consumer in the world).

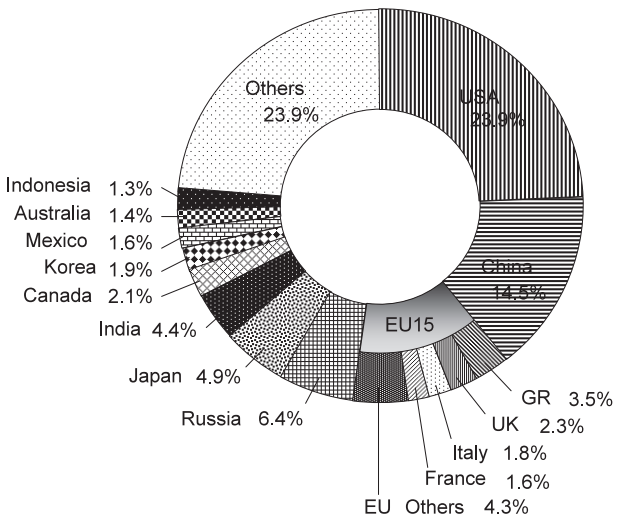

Fig. 1. Carbon Dioxide Emission in the World

Japanese institute of energy and economy (2005) report of Japanese institute of energy and economy.

(14.5%) is the second largest in the world (Fig. 1).[1] However, neither country has ratified the Kyoto Protocol. East Asian countries including China have a large responsibility to reduce the emission amount of carbon dioxide.

TOXICITIES OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) AND NITROPOLYCYCLIC AROMATIC HYDROCARBONS (NPAHs)

PAHs and NPAHs are ubiquitous environmental pollutants. They are formed through incomplete combustion of fossil fuel, wood and other organic materials including automobile exhaust, domestic heating and industrial processes. Humans and animals are exposed to PAHs and NPAHs from environmental (air, water), dietary and occupational sources, and also from cigarette smoke. Many PAHs and NPAHs are carcinogenic or probably/possibly carcinogenic to humans (Table 2)[2] and the principal concern regarding exposure to PAHs or NPAHs is that they increase the risk of cancer.

HydroxyPAHs (OHPAHs) and quinoid PAHs are formed from the corresponding PAHs in the presence of cytochrome P450 enzymes (CYPs) in human and animals as well as chemically in the atmosphere. In recent years there has been increasing interest in endocrine disruptors which may cause dysfunction of human and wildlife endocrine systems leading to cancers, reproductive system abnormalities and immune system deficiencies. As for PAHs, antiestrogenic activity was observed in a yeast assay system and estrogenic activity was found in MCF-7 cells.[3–7] Yeast two-hybrid assay system based on the ligand-dependent interaction of estrogen receptor (ER) and its co-activator has been developed as a simple and effective screening biological system. This method showed that several OHPAHs having 4 rings such as 4-hydroxybenz[*a*]anthracene (4-OHBaA) and 3-hydroxychrycene (3-OHChr) had strong estrogenic activity and that several other OHPAHs having 4 rings such as 3-hydroxybenzo[*c*]phenanthrene (3-OHBcP) and 2-hydroxybenzo[*c*]phenanthrene (2-OHBcP) had strong antiestrogenic activity. In both cases, active compounds had structures similar to that of 17β-estradiol, which binds to human estrogen receptor (hER). This structure-similarity might account for their estrogenic or antiestrogenic activities.

It has been known that 9,10-phenanthrenequinone (9,10-PQ) is redox-active which can catalyze the transfer of electrons from dithiol to oxygen, generating superoxide. The consumption rate of thiol groups was proportional to the concentration of the catalytically active redox-active species in the sample.[8] Recently, we found that other ortho-quinoid PAHs such as 5,6-chrysenequinone (5,6-CQ) and benzo[*c*]phenanthrene-5,6-quinone

Table 2. Carcinogenic PAHs, NPAHs and Relating Chemicals

Group1 (carcinogenic to humans)
Benzo[*a*]pyrene,
Coal-tars, Coal-tar pitches, Wood dust, Coal-tar distillation, Coke production, Tobacco smoking and tabacco smoke, *etc*.
Group2A (probably carcinogenic to humans)
Cyclopenta[*cd*]pyrene, Dibenz[*a*, *h*]anthracene, Dibenzo[*a*, *l*]pyrene,
Creosotes, Diesel engine exhaust, High-temperature frying, Emission from, Household combustion of biomass fuel (primarily wood), Indoor emission from, Petroleum refining (occupational exposures in), *etc*.
Group2B (possibly carcinogenic to humans)
Benz[*j*]aceanthrylene, Benz[*a*]anthracene, Benzo[*b*]fluoranthene, Benzo[*j*]fluoranthene, Benzo[*k*]-fluoranthene, Benzofuran, Benzo[*c*]phenanthrene, Chrysene, Dibenz[*a*, *h*]acridine, Dibenz[*a*, *j*]acridine, 7*H*-Dibenzo[*c*, *g*]carbazole, Dibenzo[*a*, *h*]pyrene, Dibenzo[*a*, *i*]pyrene, 3,7-Dinitrofluoranthene, 3,9-Dinitrofluoranthene, 1,6-Dinitropyrene, 1,8-Dinitropyrene, 1-Hydroxyanthraquinone, Indeno[1,2,3-*cd*]pyrene, Naphthalene, 5-Nitroacenaphthene, 6-Nitrochrysene, 2-Nitrofluorene, 1-Nitropyrene, 4-Nitropyrene,
Diesel fuel, Marine, Engine exhaust, Gasoline, Fuel oils, Residual (heavy), Gasoline, *etc*.

Cited from IARC home page (2004). Underline means PAH or NPAH.

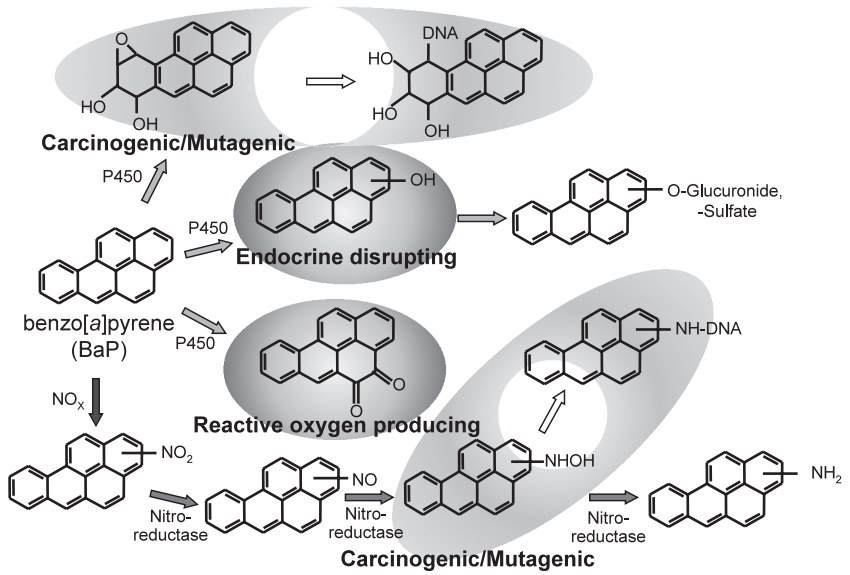

Fig. 2. Metabolic Activation of PAHs/NPAHs

(B[*c*]P-5,6-Q) also produced reactive oxygen species (ROS) as much as 9,10-PQ and that they reduced the viability of A549 cells more strongly than para-quinoid PAHs (Fig. 2).[9] These results suggest that not only carcinogenicity/mutagenicity but also endocrine disruption and the formation of ROS are also important toxicities of PAHs and NPAHs.

DETERMINATION METHODS OF PAHs AND NPAHs

Many kinds of PAHs and NPAHs are primarily formed through combustion and are emitted into the air. In addition to these compounds, heterogeneous or homogeneous reactions of parent PAHs with nitrogen oxides and hydroxyl radicals were reported for the secondary formation of several NPAHs. The partitioning of semi-volatile PAHs having no more than 3-rings between the particulate and the gas phase depends on various factors such as air temperature and the origin and properties of the aerosol. However, 4- to 6-ring PAHs, and 3- to 5-ring NPAHs are mostly associated with particulate matter.[10] Since the recognized carcinogenic PAHs and NPAHs are mostly associated with particulate matter, only particulate-bound PAHs and NPAHs were selected for analysis in this study.

Six PAHs, pyrene (Pyr), benz[*a*]anthracene (BaA), chrysene (Chr), benzo[*b*]fluoranthene

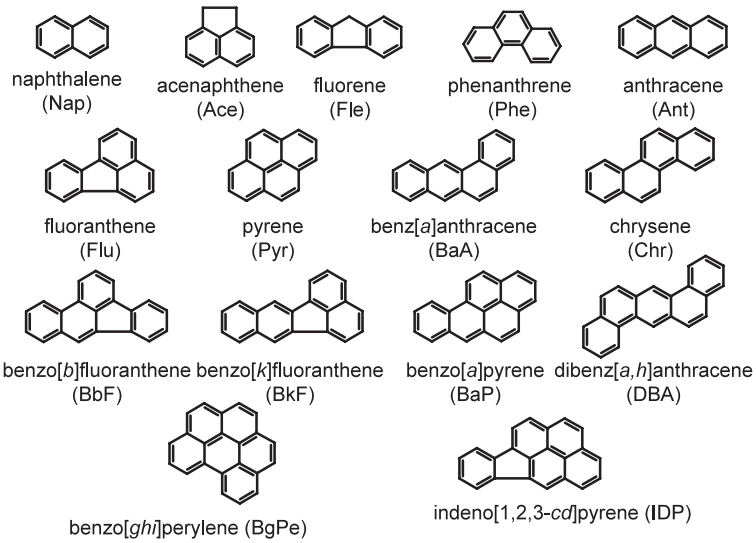

Fig. 3. Structures of Fluorescent PAHs in USEPA List

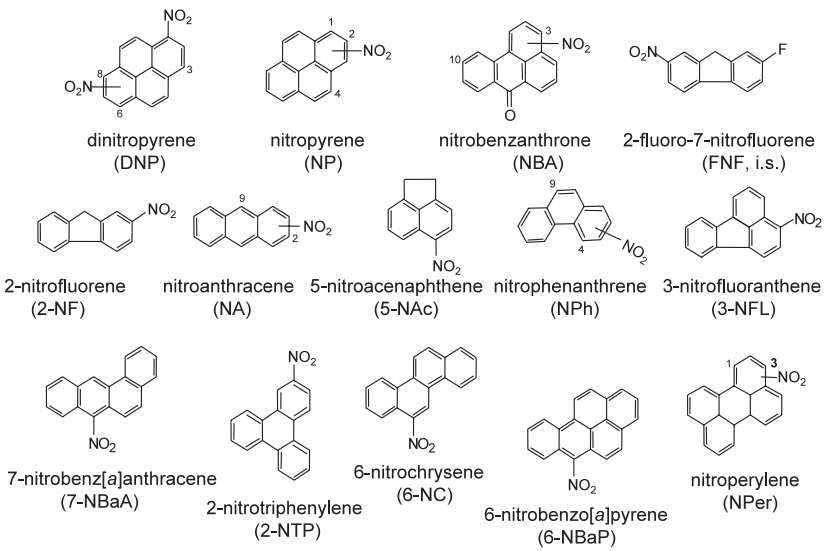

Fig. 4. Structures of Analyzed NPAHs

(BbF), benzo[*k*]fluoranthene (BkF) and benzo-[*a*]pyrene (BaP), and eleven NPAHs, 1,3-, 1,6-, 1,8-dinitrpyrene (DNPs), 1,2-nitropyrenes (NPs), 2-nitrofluoranthene (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), in the extracts from the particulates were analyzed by HPLC with fluorescence and chemiluminescence detections, respectively. The structures of those PAHs and NPAHs are respectively shown in Figs. 3 and 4 with their abbreviations. The typical chromatograms of PAHs and NPAHs in extracts from airborne particulates collected in downtown are shown in Figs. 5 and 6.[11)]

ATMOSPHERIC PAHs AND NPAHs IN EAST ASIA

We collected airborne particulates at ten cities in the Pan-Japan Sea 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 by using high-volume air samplers equipped with quartz fiber filters. The annual total PAH concentrations were in the order: Fushun > Shenyang ≃ Tieling > Beijing > Vladivostok > Kitakyushu > Sapporo > Busan > Tokyo > Kanazawa. The annual total NPAH concentrations were in the order: Fushun > Beijing > Tieling >

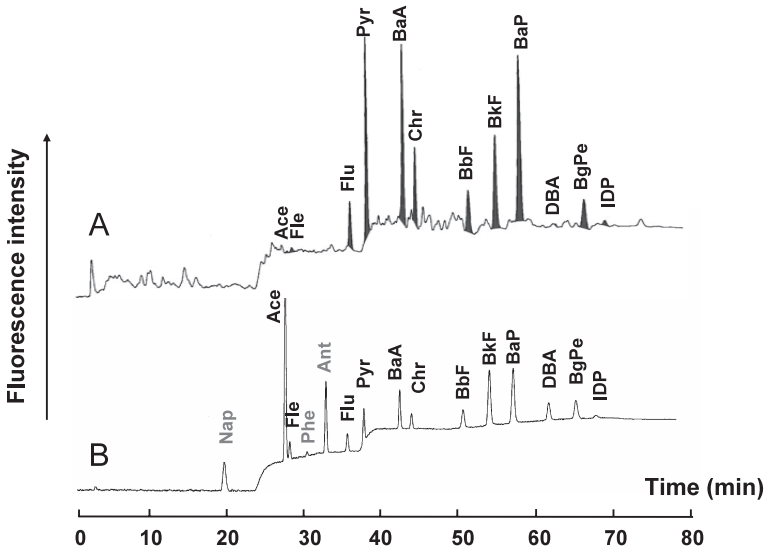

Fig. 5. Chromatograms of (A) Airborne Particulate Extract and (B) PAH Standards

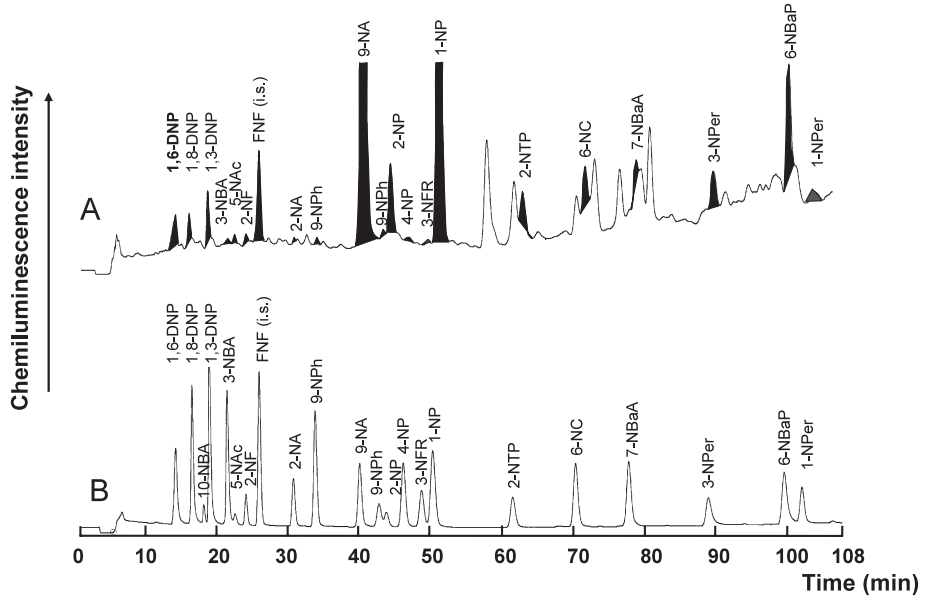

Fig. 6. Chromatograms of (A) Airborne Particulate Extract and (B) NPAH Standards

Shenyang > Tokyo > Vladivostok ≧ Kitakyushu > Sapporo > Kanazawa (Fig. 7). As shown from the numbers above columns, the concentrations of the four Chinese cities were much higher than those of the cities in the other countries. As an example, the atmospheric concentrations of PAHs and NPAHs were about 330 and 65 times higher in Fushun than those in Kanazawa, respectively. The winter to summer ratios of the concentrations of PAHs were higher than 1 in all cities and the ratios were the higher in Chinese cities than those in Japanese cities. However, the winter to summer ratios of NPAHs were not so high as that of PAHs. 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.[12–15] The significantly high concentrations of PAHs and NPAHs in China suggest the higher population of respiratory diseases such as lung cancer and asthma.

PAHs and NPAHs mainly originate from imperfect combustion of organic matter such as petroleum, coal and wood. Diesel-engine vehicles, automobiles, factories and domestic heating have been reported as sources of atmospheric

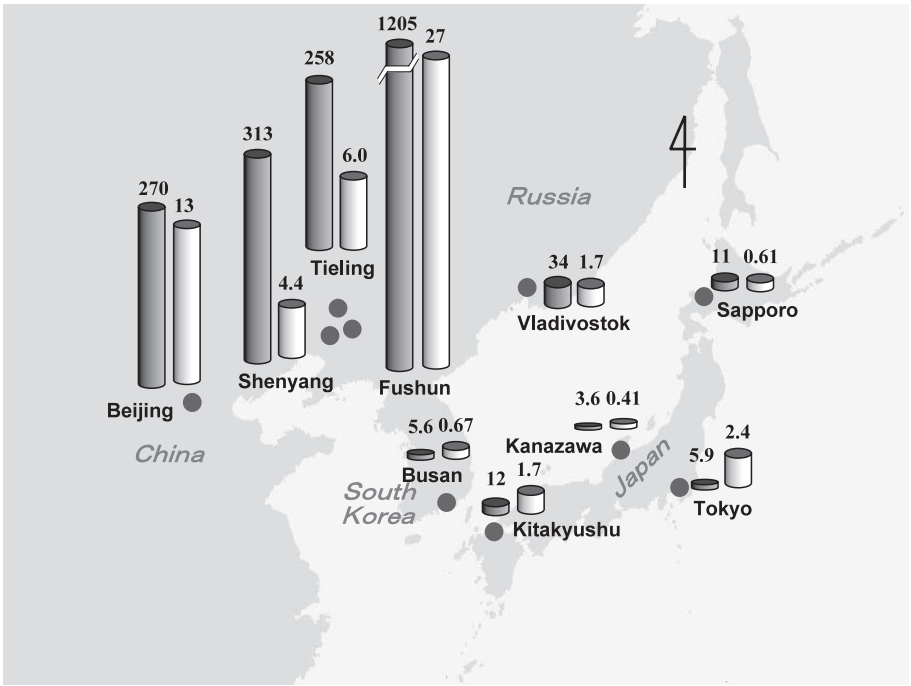

Fig. 7. Annual Average Atmospheric Concentrations of PAHs and NPAHs in East Asia

Unit: pmol m^{-3}. [PAHs] = [Pyr] + [BaA] + [Chr] + [BbF] + [BkF] + [Benzo[*a*]pyrene]. [NPAHs] = [1,3-Dnp] + [1,6-Dnp] + [1,8-Dnp] + [9-NA] + [1-Nitropyrne] + [2-NFR + 2-Nnitropyrne] + [6-Nc] + [7-NBaA] + [6-NBaP] + [3-Nitroperyrne]

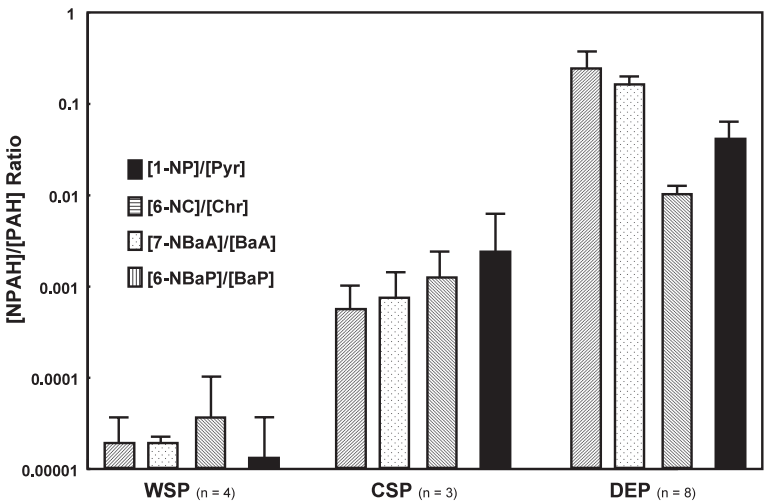

Fig. 8. [NPAH]/[PAH] Ratios of Diesel-Engine Exhaust Particulates (DEP), Coal-Smoke Particulates (CEP) and Wood-Smoke Particulates (WEP)

PAHs and NPAHs in urban areas. Since PAHs are partly nitrated in the presence of nitrogen oxides at high temperature, the yield of NPAHs from the corresponding PAHs increases with increasing temperature. The combustion temperatures in wood stove, coal stove and diesel-engine were 500–600°C, 900–1100°C and 2700–3000°C, respectively. The concentration ratios of NPAHs and corresponding PAHs, [1-NP]/[Pyr], [6-NC]/[Chr], [7-NBaA]/[BaA] and [6-NBaP]/[BaP], were in the increasing order: wood burning particulates < coal burning particulates < diesel engine exhaust particulates (Fig. 8).[10] This result is in accordance with the order of combustion temperature described above. Putting the fact into the consideration that the major contributors of combustion particulates in the atmosphere are automobiles and coal combustion systems such as city or domes-

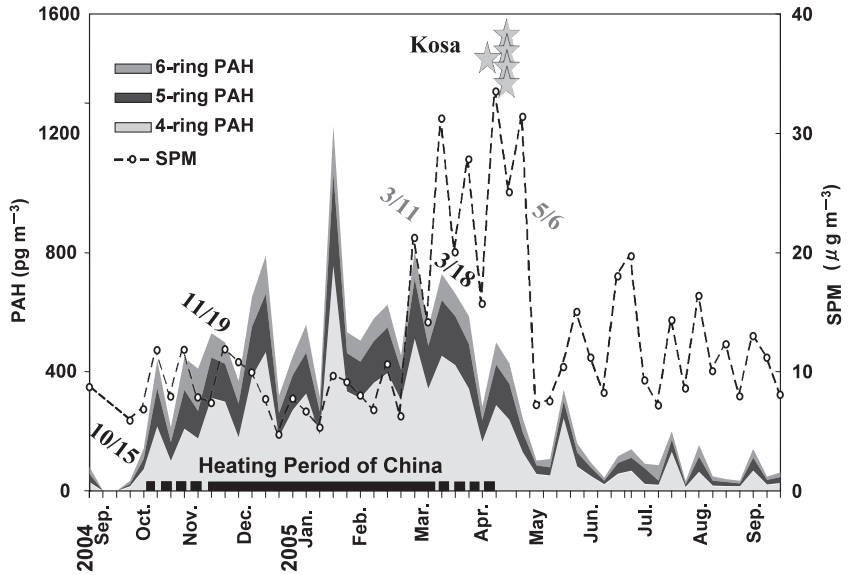

Fig. 9. Time Course of Atmospheric PAH and Particulate Concentrations at Wajima

tic heating and industries in East Asian countries, the [NPAHs]/[PAHs] concentration ratios in Fig. 7 suggest that the major contributors of PAHs and NPAHs are automobiles (mainly diesel-engine vehicles) in Japanese and Korean cities (Tokyo, Sapporo, Kanazawa and Seoul), automobiles and coal combustion systems in Russian (Vladivostok) and Chinese (Beijing) cities, and mainly coal combustion systems in the rest Chinese cities (Shenyang, Tieling and Fushun).

LONG-RANGE TRANSPORT OF PAHs AND NPAHs IN EAST ASIA

Airborne particulates were collected at Wajima, on the Noto Peninsula, Ishikawa, Japan by a high volume air sampler with a quartz fiber filter every week from September 17, 2004 to September 16, 2005. PAHs and NPAHs were analyzed by HPLC with fluorescence and chemiluminescence detections described above, respectively. The atmospheric concentrations of nine PAHs having four, five and six-rings at Wajima were all higher during the period from mid October to mid April than those in the other period. This period was not the same as the period when the concentration of suspended particulate matter was higher (from March to May) but the same as the period when a lot of coal was burned for heating in China (Fig. 9). Cluster analysis of nine PAHs and the [1-nitropyrene]/[pyrene] ratio indicated a Chinese origin of the PAHs and NPAHs. A back trajectory analysis indicated that the air samples collected in this period at Wajima were transported mainly from Northeast China over the Japan Sea (Fig. 10). These results strongly suggest that the PAHs and NPAHs detected at Wajima were long-range transported from China.[16)]

RECENT TENDENCY OF AIR POLLUTION OF PAHs AND NPAHs IN EAST ASIA

In order to determine the change of air pollution levels of PAHs and NPAHs in East Asia, atmospheric concentrations of six PAHs (Pyr, BaA, Chr, BbF, BkF, BaP) and four NPAHs (1,3-DNP, 1-NP, 6-NC, 6-NBaP) in Beijing in winter of 2004 and 2008 were compared. Although there was only four years between the two sampling times, the Beijing Olympic Games were held in August, 2008 and the sampling in winter, 2008 was just 6 months before the games. The total concentration of the six PAHs of 2008 was 7/8 of that of 2004, while the total concentration of the four NPAHs of 2008 decreased to 1/5 of that of 2004. As described above, Beijing is one of typical cities of which major contributors to atmospheric PAHs and NPAHs are coal-combustion systems and automobiles. For these reasons, Chinese government has reduced the use of coal, removed the old chimneys, and controlled the traffic transportation.

The finding that the decrease of the PAHs level was only 1/8 suggests that the countermeasures to decrease the amount of exhausted particulates from

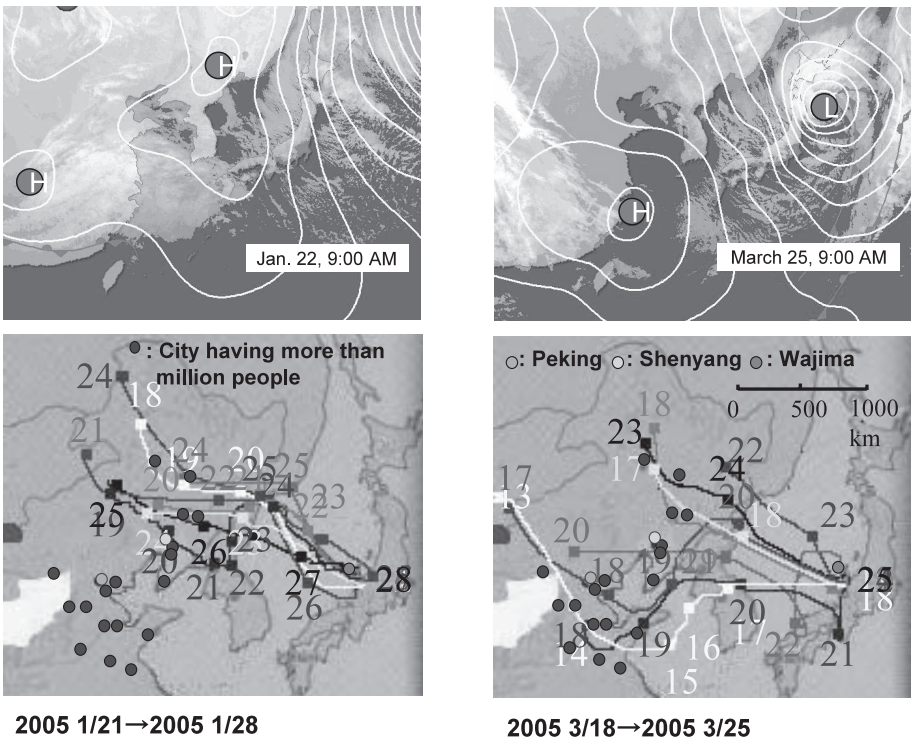

Fig. 10. Back Trajectory Analysis and Weather

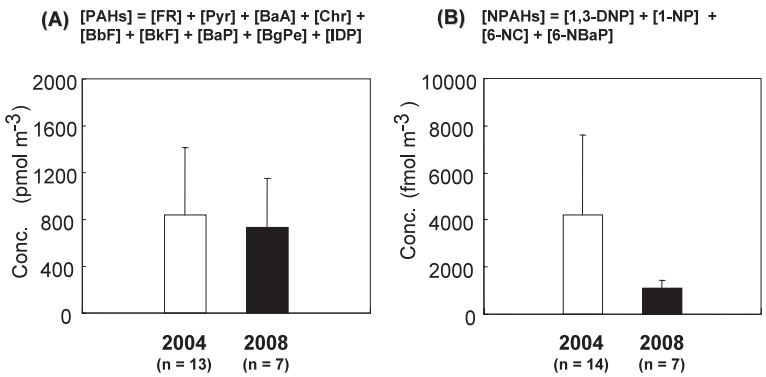

Fig. 11. Comparison of PAH/NPAH Concentrations at Beijing in Winter, 2004 and 2008

coal-combustion systems were not effective during this period. On the other hand, the PAHs level decreased by 4/5, which suggests that the countermeasures to decrease the amount of exhausted particulates from automobiles was effective (Fig. 11).[17] During the four years, the standard level of NOx exhausted from automobiles became lower and the traffic of major roads was controlled, for example, by odd/even number plates of vehicles. The similar improvement in air pollution levels of PAHs and NPAHs to that in Beijing was observed not only in other Chinese cities but also in Japanese cities, although the reason for the improvements were different in each city.

CONCLUSIONS

Because global warming prevents a crisis situation for human race, international initiatives such as the Kyoto Protocol are being considered. However, several countries that produce large amounts of exhaust (the U.S.A., China and India) are not participating in these initiatives. The failure of these countries to meet their responsibility to the abate the emission of the greenhouse gas is a big problem. Hazardous chemicals such as PAH/NPAH are generated along with the combustion of oil and coal, etc. The major contributor of these pollutants is automobiles in Japanese cities. On the con-

trary, the major contributor of these compounds in Chinese cities is coal combustion since they consume a large amount of coal in heating facilities and the factory. This causes serious air pollution and the health effect of these pollutants is a great concern. These pollutants emitted from Chinese cities are long-range transported and a part of them reaches our country. China is taking measures to reduce these sources, and as a result the air pollution levels are being gradually decreasing.

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