Distribution and Major Contributors of Polycyclic Aromatic Compounds in Particulates in Pan-Japan Sea Area

Distribution and Major Contributors of Polycyclic Aromatic Compounds in Particulates in Pan-Japan Sea Area

Ning TANG[a] , Kenji TAMURA[b] , Tetsuyuki HATTORI[c] , Xiao-Yang YANG[d] , Takayuki KAMEDA[e] , Akira TORIBA[f] and Kazuichi HAYAKAWA[g]

(a) (c) (d) (e) (f) (g) Graduate School of Natural Science and Technology, Kanazawa University,Kakuma-machi,Kanazawa,Ishikawa,920-1192,JAPAN
(b) National Institute for Environmental Studies, 16-2, Onogawa, Tsukuba, 305-8506, Japan

Urban atmospheres contain various kinds of organic pollutants. Among them, several polycyclic aromatic hydrocarbons (PAHs) and nitropolycyclic aromatic hydrocarbons (NPAHs) are carcinogenic and/or mutagenic. Recently, several PAHs have also been reported to exhibit antiestrogenic and/or antiandrogenic activities. PAHs and NPAHs in the atmosphere mainly originate from imperfect combustion of organic matters such as petroleum and coal. PAHs with 4 or more rings and NPAHs were detected in particulates from both diesel- and gasoline-engine vehicles while PAHs having lower molecular weights were detected in unburned diesel fuel. PAHs and NPAHs were also detected in smoke from steel and iron factories, and in wastewater and sediments. In addition to these sources, heterogeneous or homogeneous reactions of parent PAHs with nitrogen oxides and hydroxyl radicals were reported for the formation of 2-nitropyrene (2-NP) and 2-nitrofluoranthene (2-NFR) in the atmosphere.

In recent years the consumption of petroleum and coal has grown considerably in developing countries in the Pan-Japan sea area. The main energy source in Japan and Korea is petroleum while in China and the far-eastern part of Russia it is coal. However, only a few studies have examined the emission and behavior of atmospheric PAHs and NPAHs in these countries. In our previous studies, we have reported the following results on atmospheric PAHs and NPAHs in the cities in the Pan-Japan Sea area: (1) In the Japanese cities of Kanazawa, Sapporo and Tokyo, high correlation coefficients between the atmospheric concentrations of PAHs and NPAHs and traffic volume suggested that automobiles were the major source. Furthermore, the concentration ratios of total 1,3-, 1,6- and 1,8-dinitropyrenes to 1-nitropyrene ([DNPs]/[1-NP]) were close to the ratio typical of diesel-engine exhaust particulates, and the [DNPs]/[1-NP] ratios decreased as the percentage of diesel-engine vehicles decreased. These results suggested that, in these cities, diesel engine vehicles were the main contributors of atmospheric suspended particulates (which contain high concentrations of PAHs and NPAHs). (2) Atmospheric concentrations of PAHs in Vladivostok, Russia were one order of magnitude higher than those in Kanazawa, Sapporo, Tokyo and Kitakyushu (Japanese cities). (3) By contrast, NPAHs levels in Vladivostok were the same as those in Japanese cities.

In this study, airborne particulates were collected in seven cities in the Pan-Japan Sea countries, Shenyang (China), Vladivostok (Russia), Seoul (South Korea), Kitakyushu, Kanazawa, Tokyo and

[a] Electronic Address: tou@p.kanazawa-u.ac.jp

[b] Electronic Address: ktamura@nies.go.jp

[c] Electronic Address: thattori@p.kanazawa-u.ac.jp

[d] Electronic Address: yang@p.kanazawa-u.ac.jp

[e] Electronic Address: kameda@p.kanazawa-u.ac.jp

[f] Electronic Address: toriba@p.kanazawa-u.ac.jp

[g] Electronic Address: hayakawa@p.kanazawa-u.ac.jp

Sapporo (Japan), in winter and summer from 1997 to 2002 (Figure 1). In addition, particulates from

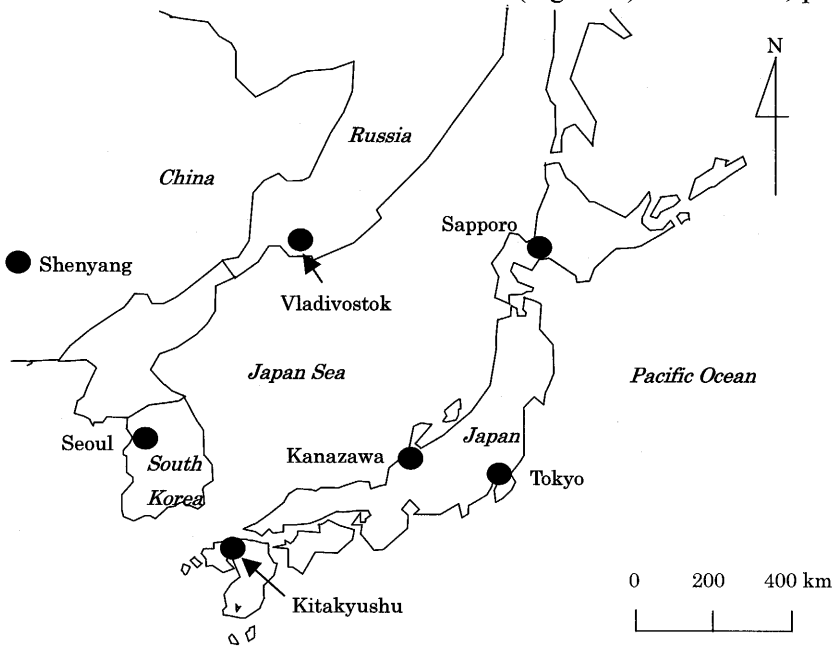

Figure 1. Sampling cities in the Pan-Japan Sea area.

domestic coal-burning heaters and diesel engine automobiles were collected in Shenyang and Kanazawa, respectively. Our objective was to clarify the typical compositions of atmospheric PAHs and NPAHs in order to identify the major sources of urban particulates.

Nine PAHs and four NPAHs in the extracts from the particulates were analysed by HPLC with fluorescence and chemiluminescence detections, respectively. The PAHs were fluoranthene, pyrene (Pyr), benz[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, benzo[*ghi*]perylene and indeno[1,2,3-*cd*]pyrene, and NPAHs were 1,3-, 1,6-, 1,8-DNPs, and 1-NP. Mean atmospheric concentrations of PAHs in Shenyang and Vladivostok were substantially higher than those in Seoul, Tokyo, Sapporo, Kitakyushu and Kanazawa. However, the mean atmospheric concentrations of NPAHs were at the same levels in all cities except Kitakyushu. The expected seasonal variations (greater PAH and NPAH concentrations in winter than in summer) were observed in all cities. In order to study the major contributors of atmospheric PAHs and NPAHs, both cluster analysis and factor analysis were used and three large groups were identified. Group 1, including Shenyang (winter), Vladivostok (winter), Kitakyushu (winter) and Kitakyushu (summer), seemed to be affected by particulates emitted from coal stoves. Group 2, including Shenyang (summer) and Vladivostok (summer), seemed be affected by both coal combustion and diesel-engine vehicles. Group 3, including Seoul (winter), Kanazawa (winter), Kanazawa (summer), Tokyo (summer), Tokyo (winter), Sapporo (summer) and Sapporo (winter), was most affected by particulates emitted from diesel-engine vehicles. Furthermore, the concentration ratios of 1-NP to Pyr were significantly smaller in Shenyang, Vladivostok and Kitakyushu and the values were close to those observed in particulates from coal stove exhaust. By contrast, in Seoul, Kanazawa, Tokyo and Sapporo the [1-NP]/[Pyr] ratio reached values similar to those of particulates released from diesel-engine automobiles. The [1-NP]/[Pyr] concentration ratio seemed to be a suitable indicator of the contribution made by diesel-engine vehicles and coal combustion to urban air particulates.