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Polycyclic aromatic hydrocarbons and nitropolycyclic aromatic hydrocarbons in urban air particulates and their relationship to emission sources in the Pan–Japan Sea countries

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Abstract

Airborne particulates were collected in seven cities in the Pan–Japan Sea countries, Shenyang (China), Vladivostok (Russia), Seoul (South Korea), Kitakyushu, Kanazawa, Tokyo and Sapporo (Japan), in winter and summer from 1997 to 2002. In addition, particulates from domestic coal-burning heaters and diesel engine automobiles were collected in Shenyang and Kanazawa, respectively. Nine polycyclic aromatic hydrocarbons (PAHs) and four nitropolycyclic aromatic hydrocarbons (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-dinitropyrenes, and 1-nitropyrene (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 clusters were identified. 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.

Keywords: NPAHs; PAHs; Airborne particulate; Contributor; Cluster analysis; Factor analysis

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1. Introduction

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 (Ames et al., 1975; Epstein et al., 1979). Recently, several PAHs have also been reported to exhibit antiestrogenic and/or antiandrogenic activities (Kizu et al., 2000). 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 (Masclet et al., 1986; Hayakawa et al., 2000). PAHs and NPAHs were also detected in smoke from steel and iron factories (Yang et al., 2002), and in wastewater and sediments (Jonker and Koelmans, 2002). 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 (Arey et al., 1986).

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 (Tang et al., 2002a, b; Ho and Lee, 2002). 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 (Hayakawa et al., 1995; Kakimoto et al., 2000). 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 (Murahashi et al., 1995). 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) (Tang et al., 2002a; Kakimoto et al., 2002). (3) By contrast, NPAHs levels in Vladivostok were the same as those in Japanese cities (Tang et al., 2002b; Kakimoto et al., 2002).

In this study, airborne particulates were collected anew in Shenyang, China and Seoul, Korea, Vladivostok, Russia and four Japanese cities, Sapporo, Kanazawa, Tokyo and Kitakyushu. Our objective was to clarify the typical compositions of atmospheric PAHs and NPAHs in order to identify the major sources of urban particulates.

2. Experimental

2.1. Sampling and characteristics of test cities

Fig. 1 shows the locations of the seven sampling cities. Their populations and numbers of registered cars are shown in Table 1. Airborne particulates were collected at 1–3 sites in each city, using high-volume air samplers at a flow rate of $1000\,L\,min^{-1}$ (Kimoto Electric Company Limited, Osaka, Japan) or low-volume air samplers at a flow rate of $28.3\,L\,min^{-1}$ (Shibata Sci. Tech., Tokyo, Japan). A heavy traffic site, a medium traffic site and a light traffic site were selected in Shenyang. A heavy traffic site and a light traffic site were selected in Vladivostok, Sapporo, Kanazawa, Tokyo and Kitakyushu. A light traffic site was selected in Seoul. Airborne particulates were collected in Seoul in 2002, in Shenyang in 2001, in Vladivostok and Kanazawa in 1999, in Kitakyushu, Tokyo and Sapporo in 1997. Air samples were collected both in winter and summer except in Seoul, where samples were collected only in winter. Airborne particulates were collected on quartz fiber filters (2500QAT-UP, Pallflex Products, Putnam, CT, USA). Air was sampled for at least a week at a time, and filters were replaced every day (high-volume air sampler) or every seven days (low-volume air sampler). Three filters in Shenyang, seven filters in Vladivostok and Kanazawa, ten filters in Sapporo,

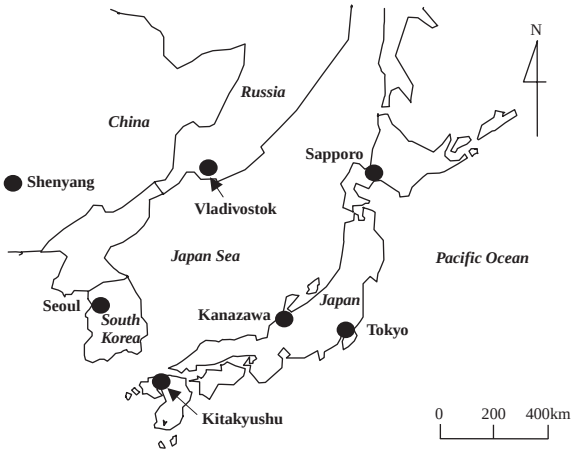

Fig. 1. Sampling cities in the Pan–Japan Sea area.