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# Comparison of Composition of Atmospheric Polycyclic Aromatic Hydrocarbons and Nitropolycyclic Aromatic Hydrocarbons in East Asian Cities

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**Abstract** - Airborne particulates were collected in seven East Asian cities, Shenyang (China), Vladivostok (Russia), Seoul (South Korea), Kitakyushu, Kanazawa, Tokyo and Sapporo (Japan). The compositions of nine polycyclic aromatic hydrocarbons (PAHs) and four nitropolycyclic aromatic hydrocarbons (NPAHs) of Shenyang and Vladivostok were similar to those in particulates emitted from domestic coal-burning heaters, while the compositions of Seoul and Japanese commercial cities were similar to those of particulates emitted from diesel-engine vehicles. These results suggest that the main sources of PAHs and NPAHs were different in these cities.

## I. Introduction

Several polycyclic aromatic hydrocarbons (PAHs) such as benzo[*a*]pyrene (BaP) and nitropolycyclic aromatic hydrocarbons (NPAHs) such as 1,3-, 1,6- and 1,8-dinitropyrenes (DNPs) are carcinogenic and/or mutagenic [1, 2]. Recently, we have found that several PAHs also had endocrine disrupting activities [3]. PAHs and NPAHs in the atmosphere were mainly originated from imperfect combustion of organic matters such as coal and petroleum. We showed that automobiles were the major contributor of DNPs and 1-nitropyrenes (NP) in the atmosphere of commercial cities in Japan using a highly sensitive HPLC/CLD method [4]. However, the compositions of atmospheric PAHs and NPAHs in an industrialized city were different from those in commercial cities, suggesting other contributors such as steel manufacturing plants using coke [5].

On the other hand, the consumption of energy sources including coal and petroleum has been increasing in developing countries in East Asia in recent years. However, only a few studies have examined the emission and behavior of atmospheric PAHs and NPAHs in these countries [6, 7]. In this study, we collected airborne particulates (AP) in Shenyang which is the largest capital city in Northeast China, Vladivostok, which is the major industrialized city in Far Eastern Russia, Seoul which is a commercial city in South Korea, Kanazawa, Tokyo and Sapporo which are typical commercial cities in Japan, and Kitakyushu, which is an industrialized city in Japan. Particulates emitted from domestic coal heaters (CEP) and diesel-engine vehicles (DEP) were also collected in Shenyang and Kanazawa, respectively. We determined nine PAHs and four NPAHs in the extracts from particulates and compared their compositions. Our results suggest that the compositions of atmospheric PAHs and NPAHs were different in these cities and that the major contributor to atmospheric PAHs and NPAHs is coal combustion in Shenyang, Vladivostok and Kitakyushu, and diesel-engine vehicles in Seoul and Japanese commercial cities.

## II. Experiment

### A. Sampling

The locations of the seven cities examined in this study are shown in Fig. 1. Air was sampled with either high- or low-volume air samplers at heavy traffic and residential sites in each city. The residential sites were not near any major contributors such as automobiles and factories. AP was collected in Shenyang in 2001, in Seoul in 2002, in Vladivostok and Kanazawa in 1999, in Sapporo, Tokyo and Kitakyushu in 1997. The samplings were carried out in winter (January-February) and summer (July-August) in each city and airborne particulates were collected on quartz fiber filters. CEP and DEP were collected in Shenyang in 2003 and Kanazawa in 1997, respectively. After being dried in a desiccator in the dark, the filters were weighed and then stored in a refrigerator until use.

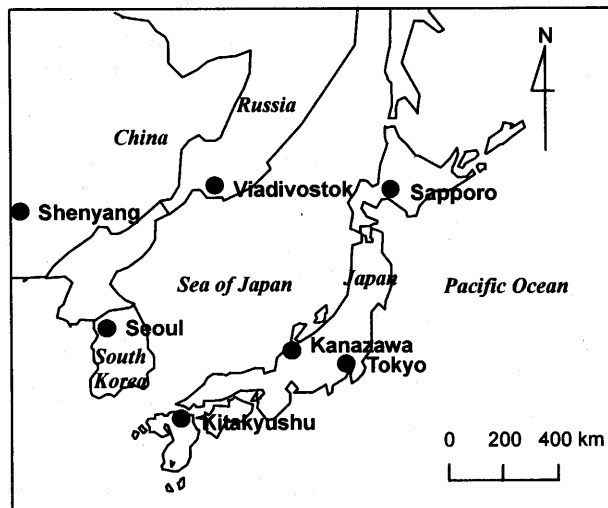


Fig. 1 Sampling cities in East Asia.

### B. Analysis and chemicals

The filter samples were pretreated and analyzed by using HPLC with fluorescence and chemiluminescence detections according to our previously reports [8, 9]. The compounds analyzed included nine kinds of PAH listed up by US EPA (fluoranthene (FR), pyrene (Pyr), benz[*a*]anthracene (BaA), chrysene (Chr), benzo[*b*]fluoranthrene (BbF), benzo[*k*]fluoranthrene (BkF), BaP, benzo[*ghi*]perylene (BgPe) and Indeno[1,2,3-*cd*]pyrene (IDP)) and four kinds of strongly mutagenic NPAHs (1,3-, 1,6-, 1,8-DNPs and 1-NP).

## III. Results and discussion

### A. Concentrations of PAHs and NPAHs in AP, CEP and DEP

The total atmospheric concentrations of the nine PAHs were in the order, Shenyang (461 pmol/m<sup>3</sup>) > Vladivostok (116 pmol/m<sup>3</sup>) > Seoul (33.4 pmol/m<sup>3</sup>) > Tokyo (24.5 pmol/m<sup>3</sup>) ≈ Sapporo (23 pmol/m<sup>3</sup>) ≈ Kitakyushu (20.5 pmol/m<sup>3</sup>) > Kanazawa (9.97 pmol/m<sup>3</sup>) (Fig. 2A). The total concentrations of DNPs (1,3-DNP + 1,6-DNP + 1,8-DNP) and 1-NP were in the order, Sapporo (582 fmol/m<sup>3</sup>) > Seoul (578 fmol/m<sup>3</sup>) > Shenyang (497 fmol/m<sup>3</sup>) > Tokyo (302 fmol/m<sup>3</sup>) > Kanazawa (133 fmol/m<sup>3</sup>) > Kitakyushu (46 fmol/m<sup>3</sup>) (Fig. 2B). This order is different from the order of PAHs, suggesting that the main sources of atmospheric PAHs and NPAHs were different in these cities.

Coal and petroleum combustions are the most important sources of PAHs and NPAHs in the atmosphere. As primary energy source, petroleum is popular in Japanese commercial cities and Seoul, while coal is used in Shenyang and Vladivostok. In Shenyang, for example, about ten million tons of coal is consumed every year for factories, thermal power plants and residential heating. In this study, we collected particulates exhausted from four typical coal stoves in Shenyang in winter and from three typical diesel-engine vehicles in Kanazawa. The concentration of the total nine PAHs in CEP was

about 7 times higher than that in DEP (Fig. 2A), while the concentration of the total four NPAHs in CEP was about 40 times higher than that in DEP (Fig. 2B). The nitration may be lower during coal combustion because the combustion temperature and amount of oxygen in coal stoves and boilers are lower than those in diesel engines.

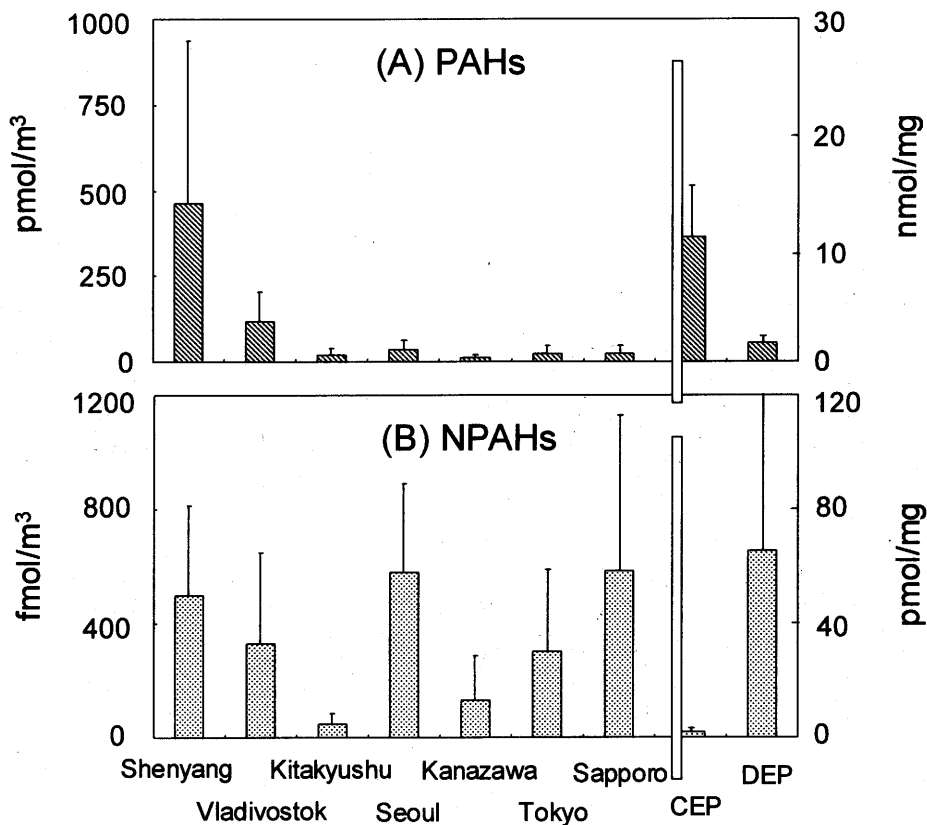


Fig. 2 Concentrations of (A) nine PAHs and (B) four NPAHs in seven cities ( $\text{pmol/m}^3$ ,  $\text{fmol/m}^3$ ) and in CEP and DEP ( $\text{nmol/mg}$ ,  $\text{pmol/mg}$ ).

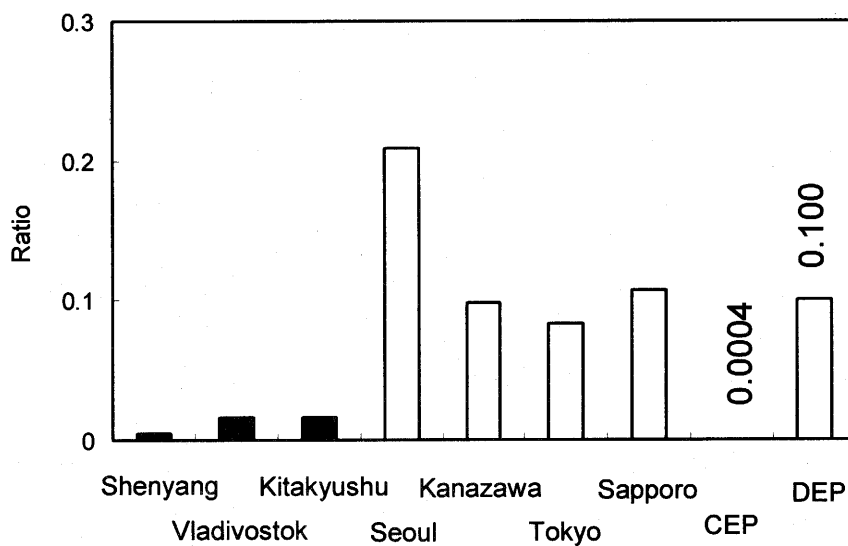


Fig. 3 Concentration ratios of 1-NP to Pyr in AP, CEP and DEP

## B. Compositions of PAHs and NPAHs

In order to clarify the main contributor of atmospheric PAHs and NPAHs in these cities, we calculated the concentration ratios of several PAHs and NPAHs in CEP and DEP. The [1-NP]/[Pyr] ratios of CEP and DEP were 0.0004 and 0.100, respectively. The large difference of the values between CEP and DEP suggested that [1-NP]/[Pyr] ratio is an useful indicator of not only diesel-engine vehicles but also coal combustion. The [1-NP]/[Pyr] ratios of airborne particulates of the seven cities were also calculated. In Fig. 3, the ratio was 0.004 at Shenyang, 0.016 at Vladivostok and 0.015 at Kitakyushu. These smaller ratios might be strongly affected by CEP. On the other hand, the ratio was 0.082 at Tokyo, 0.098 at Kanazawa, 0.107 at Sapporo and 0.208 at Seoul. The larger ratios might be strongly affected by DEP. These results showed that the main contributor of atmospheric PAHs and NPAHs was coal combustion in Shenyang, Vladivostok and industrialized area in Kitakyushu, while the main contributor was petroleum combustion in Tokyo, Sapporo, Kanazawa and Seoul.

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