Environmental behaviors of polycyclic aromatic hydrocarbons and nitropolycyclic aromatic hydrocarbons in the Pan-Japan Sea area

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Dissertation abastract

Many kinds of polycyclic aromatic hydrocarbons (PAHs) and nitropolycyclic aromatic hydrocarbons (NPAHs) originated from the imperfect combustion of the fossil fuels such as coal and oil. Some of them show strong carcinogenicity/mutagenicity and endocrine disrupting activity. This research is focusing on the generation and atmospheric behavior of PAHs and NPAHs in Pan-Japan sea area. Atmospheric particulates were sampled in several cities of Pan-Japan sea area (Kanazawa, Sapporo, Tokyo, Beijing, Pusan, and Vladivostok) in all seasons. By analyzing these samples, differences of PAHs and NPAHs compositions and sources in those cities were investigated. As a result, coal burning exhaust is the main emission source in Beijing and Vladivostok, while in Busan and Japanese cities atmospheric PAHs and NPAHs were mainly from diesel vehicles. Furthermore, a sampling campaign was also performed at "Kanazawa University Wajima Sampling Station" for the research about the long-range transport of air pollutants. Based on one year's data, it was clarified that PAHs at Wajima were influenced by the air from the Asian continent during the heating period of China. In addition, the concentration of water-soluble fluoride at Wajima was high in both the heating period of China and the period of the Asian Dust. This indicated that fluorides were influenced by not only coal burning exhausts from the Asian continent but also the Asian Dust.

【Background】

Polycyclic aromatic hydrocarbons (PAHs) and nitropolycyclic aromatic hydrocarbons (NPAHs) are ubiquitous pollutants. Some of them are carcinogenic or mutagenic or have endocrine-disrupting activity. PAHs and NPAHs in the atmosphere are mainly originated from imperfect combustion of fossil fuels such as coal and oil. Different types of energy sources are coexisting in Pan-Japan Sea area. The main energy source is oil in Japan and Korea, while in China and Far Eastern Russia it is coal. In addition, countries in this area except Japan have big population and are accomplishing a remarkable change with industrial development. In recent years, with the increasing of the fossil fuel consumption and traffic volume, air quality has become worse with large quantity of pollutants such as combustion particulate matters in urban air.

In this study, airborne particulate matters (PM) were collected seasonally in four countries' cities (Beijing, Vladivostok, Busan, Kanazawa, Sapporo, Tokyo and Kitakyushu) in Pan-Japan Sea area (Fig. 1). By analyzing PAHs and NPAHs in the extracts from those samples, the differences of air pollution status of PAHs and NPAHs in each city caused by different energy structures, traffic conditions and life styles were investigated. In addition, the temporal variation of PAHs and NPAHs pollution level and main emission sources were clarified by comparing with previous data obtained 6-8 years ago. Furthermore, the long-range transport of PAHs and fluoride originated in the Asian continent to Japan was also investigated by continuously monitoring throughout one year at Noto peninsular, at the suburban of Wajima city, Ishikawa prefecture, Japan.

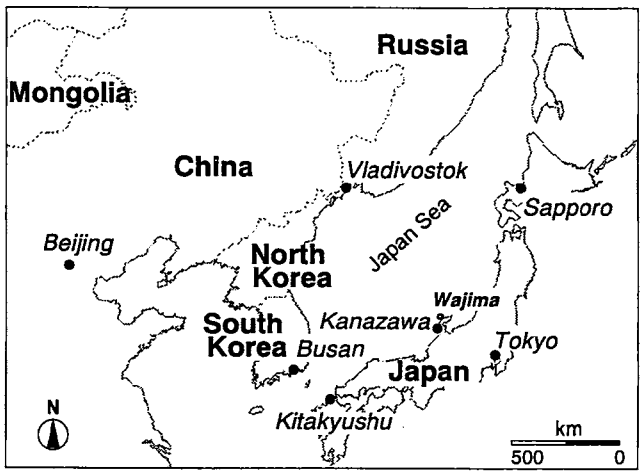

Fig. 1 Sampling sites

【Experimental】

PM were collected seasonally from 2004 to 2005 by a high volume air sampler with a quartz filter at one or two sites in each of seven Pan-Japan Sea cities (Beijing, Vladivostok, Busan, Kanazawa, Sapporo, Tokyo and Kitakyushu). PAHs and NPAHs in those samples were extracted in to organic solution. PAHs and NPAHs were analyzed by HPLC with fluorescence detection and HPLC with chemiluminescence detection, respectively. In addition, PM were also collected at Kanazawa University Wajima Sampling Station throughout one year (2004-2005). PAHs in the extract were determined and water-soluble fluoride ion was analyzed by ion chromatography.

【Result and discussion】

The air pollution by PAHs and NPAHs was much heavier in Beijing than those in the other Pan-Japan sea cities. The concentrations in Japanese cities were the lowest and at the similar levels to that of Busan. Regulation of the smoke emission was severe and de-particle measures were performed well in Japan. On the other hand, relevant countermeasures were not enough in China, where the heavy atmospheric pollution was observed in urban area recently. Therefore, in order to identify the emission sources of PAHs and NPAHs, the concentration ratio of NPAH to its mother PAH which related to the burning temperature was used in this study. As a result, diesel-engine vehicle was the main emission source in Sapporo (summer and winter), Kanazawa (summer and winter) and Busan (spring). And coal burning emission was the biggest contributor of PAHs and NPAHs in Beijing and Vladivostok in winter. In other cities, PAHs and NPAHs were from both diesel-engine exhausts and coal burning. And the influences by gasoline vehicles or factories also should not be neglected. When compared the data obtained this work to those from previous study, PAHs and NPAHs decreased in Vladivostok and Japanese cities except Kitakyushu. It is probably owing to the decreasing of the number of diesel cars and also because of a performance enhancement of the effluent gas depurator of automobiles.

The atmospheric concentrations of PAHs at Wajima showed at a high level from Oct. 15, 2004 to Apr. 14, 2005 which coincident with the heating period of

China (Fig. 2). And during this heating period, the composition of PAHs at Wajima was close to that at Shenyang, a big city in Northeastern China, by a statistic method (Principal Component Analysis). Back trajectory analysis indicated that the air mass collected at Wajima during this heating period was passed through Northeast China. These results suggest that PAHs emitted in the Asian continent during the heating period were transported over long distances to Japan.

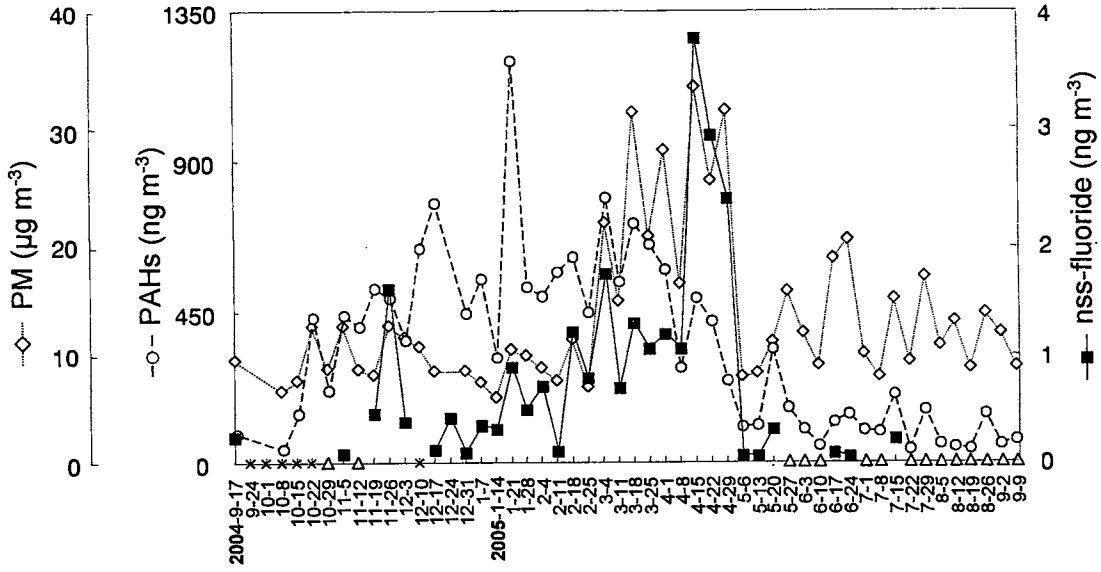

Fig. 2 Variations of PM, PAHs and nss-fluoride at Wajima. Dates indicate the first day of a 7-day sampling period. (×: not detected; Δ: detected but less than detection limit for nss-fluoride).

On the other hand, atmospheric non-sea-salt fluoride (nss-fluoride) ion was also showed a high concentration level during the heating period and especially during the period of the Asian Dust (Apr., 2005) (Fig. 2). Only slight correlation was observed between fluoride and PAHs. As the reason of this, firstly, fluoride was not only exhausted from coal burning heating system, but also was included in the particulates of the Asian Dust themselves in the arid area of Northeast Asian continent. And another reason probably is the behaviors of PAH in the atmosphere, such like chemical reactions, are more complicated than inorganic ion, fluoride.

学位論文審査結果の要旨

［審査経過］審査方針に従い，基礎学力を確認し，各委員による面接と諮問を行った。１月２９日に口頭発表（最終試験）を行い，終了後に開催した最終審査委員会において協議の結果，次のように判定した。

［審査結果］東アジアは、著しい産業経済発展を遂げる一方で、化石燃料の大量消費により著しい大気汚染を招いている。本研究は、環日本海域における有害性多環芳香族炭化水素（PAH）及びニトロ多環芳香族炭化水素（NPAH）の大気内挙動を明らかにする目的で、わが国及び中国，韓国，ロシアの計７都市と能登半島の先端で大気粉塵を継続捕集して、PAH，NPAH を分析した。その結果、中国の都市の PAH，NPAH 濃度は，他の国の都市の値より著しく高く，主要排出源は組成の特徴から石炭燃焼施設であることを明らかにした。次に，８年前の調査結果と比較して，殆どの都市で汚染レベルは低下傾向にあることを明らかにした。さらに，能登半島の大気中 PAH は、中国の石炭暖房期間（10 月中旬～4 月中旬）に一致して濃度が上昇したこと、その時の大気塊は中国東北地方を経由してきたこと、大気の PAH 組成が能登半島と中国東北地方の都市で近似したことから、主として中国東北地方の石炭燃焼で発生した PAH が日本列島まで長距離輸送されたことを明らかにした。本論文は、環日本海域の PAH, NPAH の大気内挙動の全貌を知る大きな手掛りを与えている。よって、審査委員会は博士（薬学）に値すると判定した。