Study on Atmospheric Polycyclic Aromatic Hydrocarbons at a Background Site of Ishikawa Prefecture, Japan

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Airborne particulates were collected at Wajima in Noto peninsula, Ishikawa, Japan, every week from September 17, 2004 to June 3, 2005. Both PAHs and NPAHs in the extracts from the particulates were analysed by HPLC with fluorescence and chemiluminescence detection. During the period of central heating of China (October 15 – April 15) and the period of sandstorms detected in Wajima (April 15 – 21), atmospheric concentrations of PAHs and NPAHs increased significantly when the northwest wind was predominant at Wajima. The concentration ratio of NPAHs to PAHs was not similar to that of Japanese urban air but similar to that of Chinese urban air. The increase of the atmospheric concentrations of PAHs and NPAHs could attribute to a long-range transportation of combustion particles from China.

Key Words: polycyclic aromatic hydrocarbon, nitropolycyclic aromatic hydrocarbon, airborne particulate, long-range transportation

1. Introduction

In East Asia, with the rapid increasing of the population and the development of economy, a large amount of pollutants were emitted through the combustion of fossil fuels such as coal and oil. Sulfur dioxide, as an example, emitted from China causes acid rain in Japan, suggesting that other pollutants also would be transported to other countries located downstream of the northwest wind from the original countries. 1, 2)

In various air pollutants, many polycyclic aromatic hydrocarbons (PAHs) and nitropolycyclic aromatic hydrocarbons (NPAHs) show carcinogenicity/mutagenicity and endocrine disrupting activity. 3, 4) We reported that automobiles, especially diesel-engine vehicles, were the main contributors of PAHs and NPAHs in atmospheric particulates in Japanese and Korean cities and that PAHs and NPAHs were mainly emitted into the atmosphere through the coal combustion in Russia (Vladivostok) and China (Shenyang). 5) However, there is no report about the long-range transportation of particulates containing PAHs and NPAHs from these countries to Japan.

In this study, airborne particulates were sampled at Wajima, in order to clarify the long-range transportation of polycyclic aromatic hydrocarbons from China to Japan.

2. Experimental

2.1. Sampling

Airborne particulates were collected at Wajima Air Monitoring Station in Noto peninsula, Ishikawa, Japan, which located on the side of the Japan Sea. There is no major source of PAHs/NPAHs surrounding the station and the atmospheric conditions are easily influenced by the effect of the Asian Continent. Airborne particulate sampling was done by a high volume air sampler (AH-600, Shibata Japan) with a quartz filter (8 inch × 10 inch, 2500QAT-UP, Pallflex Products, Putnam, CT, U. S. A.) at a flow rate of 700 L min⁻¹ every week from September 17, 2004 to June 3, 2005, including the period of central heating of China (October 15 - April 15) and the period of sandstorms detected at Wajima (April 15 - 21). Filters were weighed under the constant temperature and humidity.

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2.2. Pretreatment and analysis of samples
The filters were cut into small pieces in a flask and then extracted ultrasonically twice with benzene/ethanol (3:1, v/v). After filtered the solution was evaporated to dryness (1000 Pa, room temperature). The residue was dissolved in acetonitrile, and then a part of the solution was injected into the HPLC system for PAHs. An internal standard was added to the rest part of the solution and dissolved in benzene/ethanol (3:1, v/v). Then it was washed with sodium hydroxide solution, sulfuric acid solution and water. At last, the solution was evaporated to dryness again. The residue was redissolved in ethanol and an aliquot was injected into the HPLC for NPAHs. The other conditions were the same as in our previous reports. 5

Ten PAH species (Benzo[ghi]perylene (BghiP), Fluoranthene (Flu), Benz[a]anthracene (BaA), Benzo[a]pyrene (BaP), Benzo[b]fluoranthene (BbF), Chrysene (Chr), Benzo[k]fluoranthene (BkF), Indeno[1,2,3-cd]pyrene (IDP), Pyrene (Pyr), Dibenz[a,h]anthracene (DBA)) were determined by using HPLC with fluorescence detection. Twenty NPAH species (1,3-, 1,6-, 1,8-dinitropyrenes (DNP), 1-, 4-nitropyrene (NP), 3-, 10-nitrobenzantrone (NBA), 2-nitrofluorene (NFR), 6-nitrochrysene (6-NC), 2-nitrotriphenylene (2-NTP), 2-nitrofluorene (2-NF), 5-nitrocyclohexadiene (5-Nc), 2-, 9-nitroanthracene (NA), 7-nitrobenz[a]anthracene (7-NBaa), 4-, 9-nitrophenanthrene (NPh), 1-, 3-nitropyrene (NPyr), 6-nitrobenzo[a]pyrene (6-NBaaP), 3-nitrofluoranthene (3-NFL)) were determined by using HPLC with chemiluminescence detection. The conditions were the same as in our previous reports. 5

2.3. Back trajectory analysis
Back trajectory analysis was done by the online program, Meteorological Data Explorer (METEX), which was developed by National Institute for Environmental Studies (NIES) and the basic meteorological data was supplied by European Center for Medium-Range Weather Forecast (ECMWF).

3. Results and Discussion
3.1. Concentrations of PAHs and AP

**Fig. 1** shows the changes of the concentrations of PAHs and airborne particulates (AP) during the sampling period at Wajima. An increase tendency of AP was observed obviously during March 11 and May 6, 2005. During this period, the yellow sands transported from the Asian Continent were detected at Wajima. On the other hand, an increasing tendency of PAHs’ concentration was observed during October 15 and November 19, 2004. And then the high concentration of PAHs was kept until March 25, 2005. After that, it showed a decreasing tendency until May 13, 2005. The period of high concentration of PAHs approximately agrees with the heating period from October 15, 2004 to April 15, 2005 for a part of Northern China and from October 15, 2004 to March 15, 2005 for the rest area of Northern China.

3.2. Compositions of PAHs and NPAHs

The concentration ratios of NPAH to its mother PAH such as [1-NP]/[Pyr], [6-NC]/[Chr], [7-NBAA]/[BaA] and [6-NBaaP]/[BaP] are quite different between coal stove exhaust particulates (CEP) and diesel-engine exhaust particulates (DEP) because the ratios depend on the combustion temperature.5 In our previous study, the [1-NP]/[Pyr] ratio of coal stove particulates was 0.001 and that of diesel-engine exhaust particulates was 0.36. 5 The much smaller ratio of airborne particulates collected at Shenyang.
Table 1  Ratios of 1-NP to Pyr at Wajima, Shenyang and Kanazawa.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Wajima</th>
<th>Shenyang</th>
<th>Kanazawa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Heating period</td>
<td>No-heating period</td>
<td>2005/1/14-1/21</td>
</tr>
<tr>
<td></td>
<td>2004/11/19-2005/3/18</td>
<td>2004/9/17-10/18 + 2005/5/6-6/3</td>
<td>n = 18</td>
</tr>
<tr>
<td>Pyr Mean±S.D. (pg/m³)</td>
<td>15.7 ± 7.1</td>
<td>7.3 ± 0.1</td>
<td>50999 ± 14455</td>
</tr>
<tr>
<td>1-NP Mean±S.D. (pg/m³)</td>
<td>0.15 ± 0.09</td>
<td>5.3 ± 0.08</td>
<td>179 ± 19</td>
</tr>
<tr>
<td>[1-NP]/[Pyr] Min</td>
<td>0.003</td>
<td>0.005</td>
<td>0.003</td>
</tr>
<tr>
<td>Max</td>
<td>0.026</td>
<td>0.129</td>
<td>0.005</td>
</tr>
<tr>
<td>Mean</td>
<td>0.011</td>
<td>0.027</td>
<td>0.004</td>
</tr>
<tr>
<td>Median</td>
<td>0.008</td>
<td>0.013</td>
<td>0.004</td>
</tr>
</tbody>
</table>

(0.003) suggests that the main contributor was coal-smoke particulates while the large ratio of airborne particulates collected at Kanazawa (0.13) suggests that the main contributor was diesel-engine exhaust particulates. In this work, the [1-NP]/[Pyr] ratio was also calculated to identify the origin of particulates collected at Wajima (Table 2). The mean and median values at Wajima (0.011, 0.008) during the heating period of China were much smaller than those at Kanazawa (0.235, 0.220) but close to those at Shenyang (0.004, 0.004), which strongly suggests that atmospheric PAHs and NPAHs at Wajima were mainly PAHs and NPAHs that had been transported from China. On the other hand, the fact that the ratios of Wajima were a bit larger than those of Shenyang suggests that Japanese domestic PAHs and NPAHs contributed to a few percentages, though the faster degradation of 1-NP than that of Pyr in the air may be considered.

3.3. Cluster analysis

Cluster analysis was performed with the Ward’s method and standardized squared Euclidean distance. The statistical analysis software program was kindly provided by Dr. Susumu Hayakari of the Aomori Prefectural Institute of Public Health and Environment (Aomori, Japan).

For the cluster analysis, as the parameter values, the concentration ratios of Flu, Pyr, BaA, Chr, BbF, BkF, BghiPe and IDP to the total PAHs respectively were

![Fig. 2 Cluster analysis of Atmospheric PAHs of Wajima (W), Shenyang (S) and Kanazawa (K)](image-url)
used. And the data of Shenyang and Kanazawa in winter were from our previous report.

Fig. 2 shows three large clusters by the cluster analysis. Cluster 1 included most samples of Wajima only expect December 10 which was included in Cluster 3. Cluster 3 mostly included Kanazawa (winter) while Cluster 2 included Shenyang (winter) only.

This result suggested that the PAHs of Wajima in winter composed consistently in accordance with those of Shenyang (winter) but a bit far from those of Kanazawa, supporting the above consideration that the atmospheric PAHs at Wajima were strongly affected by the combustion particulates transported from the Asian Continent during the heating period of China.

3.4. Back trajectory analysis

Back trajectory analysis has often been used to study the transportation of pollutants. By this method we calculated the 4-day back trajectories at 1000 m above ground level of the air to Wajima during the sampling period. Most of the traces of the samples from November 19, 2004 to March 18, 2005, which corresponds to the heating period of China, passed through Northeast China which has a high density of population and industry. The atmospheric pressure pattern in northeast Asia in winter is usually characterized by a high pressure area in the west and a low pressure area in the east. This is thought to result in long-range transportation of air from the Asian continent to Japan.

Five representative trajectories that were calculated for the period during the heating season period in China originated in northeast China (Fig. 3A). On the other hand, most of the trajectories during the no-heating period didn’t pass through the Asian continent (Fig. 3B). These results are consistent with our finding that the atmospheric PAHs and NPAHs at Wajima were strongly affected by the combustion particulates transported from the Asian Continent during the heating period of China.

4. Conclusion

The high atmospheric PAHs concentrations at Wajima were observed in the heating period of China. [1-NP]/[Pyr] ratios of Wajima were similar to those of Shenyang. The cluster analysis showed that the composition of PAHs at Wajima was close to that at Shenyang but not to that at Kanazawa. The back trajectory analysis indicated that the air was transported from the Asian Continent over the Northeast China. These results suggested strongly that PAHs and NPAHs were long-range transported from China.

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References


