Distribution of polycyclic aromatic hydrocarbons in the North-western part of the Japan Sea

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Polycyclic aromatic hydrocarbons (PAHs):

acenaphthene (Ace)  fluorene (Fle)  anthracene (Ant)
fluoranthene (Flu)  pyrene (Pyr)  benz[a]anthracene (BaA)  chrysene (Chr)
benzo[b]fluoranthene (BbF)  benzo[k]fluoranthene (BkF)  benzo[a]pyrene (BaP)  dibenz[a,h]anthracene (BaA)
benzo[g,h,i]perylene (BgPe)  indeno[1,2,3-c,d]pyrene (IDP)
Mechanisms of PAHs formation:

• **Pyrogenic** -
  very rapid, high temperature (~700°C) incomplete combustion or pyrolysis of organic materials

• **Petrogenic** -
  very slow (millions of years) rearrangement and transformation of biogenic organic materials at moderate temperatures of 100-300°C to form fossil fuels

• **Diagenic** -
  relatively rapid (days to years) transformation of certain classes of organic compounds in soils and sediments

• **Biogenic** -
  direct biosynthesis by organisms
CTD/Rosette system

Rosette with 12 pcs. of Niskin bottles (the volume is 5 or 12 liters for each) for seawater sampling

SBE 9plus Underwater Unit (Manufacturer Sea-Bird Electronics, Inc.)
Collection samples of seawater and suspended matter

**Filtration**

<table>
<thead>
<tr>
<th>Water</th>
<th>Suspended matter – SM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cartridge <strong>C18</strong> (preconditioned 5 ml EtOH, 5 ml distilled water), flow rate 10 ml/min</td>
<td></td>
</tr>
<tr>
<td>Dried under vacuum condition</td>
<td>Dried in the air about 1 h</td>
</tr>
</tbody>
</table>

Kept in the refrigerator at 4°C

At the all stations water samples were collected from the surface layer. At the station 8 water samples were collected at the following depths (m): 3480 (bottom), 3000, 2500, 2000, 1500, 1000, 500, 300, 200, 100, 50 and 33.
### PAHs extraction:

<table>
<thead>
<tr>
<th>Analysis</th>
<th>C18 (water)</th>
<th>Filter (SM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Desorption</td>
<td>15 ml dichloromethane</td>
<td>30 ml mixture benzene:ethanol 3:1</td>
</tr>
<tr>
<td>Clean up</td>
<td>Silica gel cartridge, hexane:acetone 9:1</td>
<td>5%NaOH, 20%H₂SO₄, distilled H₂O</td>
</tr>
<tr>
<td>Dry</td>
<td></td>
<td>Silica gel cartridge, hexane:acetone 9:1</td>
</tr>
<tr>
<td>Diluted in acetonitrile</td>
<td>200 µl DMSO + 800 µl acetonitrile</td>
<td>100 µl DMSO + 900 µl ethanol</td>
</tr>
</tbody>
</table>
PAHs analysis system

The HPLC system:

2 Hitachi L-2130 pumps; Hitachi degasser; Hitachi L-2485 fluorescence detector; Hitachi organizer.

Analytical column - Inertsil ODS-P (4.6i.d. × 250mm, 5μm, GL Sciences)
Guard column - Inertsil ODS-P (4.0i.d. × 10mm, 5μm, GL Sciences)

Mobile phase - mixture of acetonitrile and distilled water
Flow rate of mobile phase - 1.0 mL/min

The sample was detected by fluorescence detector for which the excitation and emission wavelengths were automatically set by a time program.
The total concentrations of PAHs in the surface samples of seawater

Total PAHs = Dissolved PAHs + PAHs sorbed on SM
Concentrations of DPAHs and SM-PAHs in the surface samples of seawater

- **DPAHs** – Dissolved PAHs
- **SM-PAHs** – PAHs sorbed on suspended matter (SM)

3-4 ring PAHs are dominated also, but concentrations of 5-6 ring PAHs are increasing from 0.11 to 0.24 ng/l for 5-ring PAHs and from 0.06 to 0.19 ng/l for 6-ring PAHs comparison with dissolved phase.
Vertical distribution PAHs at the station 8

Total concentrations of 3,4,5,6-ring and sum PAHs, ng/l

suspended solid, g

Labels meaning:
- ports of call
- PAH analysis stations
Vertical distribution of DPAHs and SM-PAHs

Concentrations of DPAHs, ng/l

Concentrations of SM-PAHs, ng/l
PAHs ratios as markers of PAHs sources:

<table>
<thead>
<tr>
<th>PAHs ratios</th>
<th>Petrogenic sources</th>
<th>Pyrogenic sources</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Petroleum</td>
<td>Coal combustion</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>combustion</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flu/(Flu+Pyr)</td>
<td>&lt;0.4</td>
<td>0.4–0.5</td>
<td>&gt;0.5</td>
<td></td>
</tr>
<tr>
<td>IDP/(IDP+BgPe)</td>
<td>&lt;0.2</td>
<td>0.2–0.5</td>
<td>&gt;0.5</td>
<td></td>
</tr>
<tr>
<td>BaA/(BaA+Chr)</td>
<td>&lt;0.2</td>
<td>0.2–0.35</td>
<td>&gt;0.35</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>15</th>
<th>16</th>
<th>18</th>
<th>19</th>
<th>20</th>
<th>21</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flu/(Flu+Pyr)</td>
<td>0,30</td>
<td>0,32</td>
<td>0,36</td>
<td>0,30</td>
<td>0,37</td>
<td>0,32</td>
<td>0,19</td>
<td>0,21</td>
<td>0,31</td>
<td>0,17</td>
<td>0,26</td>
</tr>
<tr>
<td>IDP/(IDP+BgPe)</td>
<td>0,46</td>
<td>0,53</td>
<td>0,55</td>
<td>0,49</td>
<td>0,43</td>
<td>0,45</td>
<td>0,40</td>
<td>0,46</td>
<td>0,55</td>
<td>0,47</td>
<td>0,50</td>
</tr>
<tr>
<td>BaA/(BaA+Chr)</td>
<td>0,45</td>
<td>0,48</td>
<td>0,45</td>
<td>0,40</td>
<td>0,44</td>
<td>0,45</td>
<td>0,46</td>
<td>0,49</td>
<td>0,41</td>
<td>0,43</td>
<td>0,45</td>
</tr>
</tbody>
</table>
Conclusions:

• At first time was measured the levels of PAHs in the Japan Sea (DPAHs ~2.5 to 4.8 ng/l; SM-PAHs ~1.2 to 4.4 ng/l with highest content of 3-ring PAHs)

• The main source of PAHs in the Japan Sea is the atmosphere

• The markers point to different origins of PAHs in the Japan Sea:
  crude oil, petroleum combustion, coal combustion (heating season)
Acknowledgments:

- Japan-Russian Youth Exchange Centre, Tokyo, Japan
- Kanazawa University, Kanazawa, Japan
Thank you for your attention