Monitoring Chemical Substances in Surface Sea Water in North Pacific Area

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Concentrating sampling method for trace organic chemicals in the sea water

- Dr. Kunugi (NIES, Japan) have been developing a monitoring (sampling) method trace organic chemicals in the surface sea water by using ships (ferries, etc.)
Key-words

Marine pollution Monitoring

Persistent

Long range transport : Grasshopper effects

Voluntary observation ships(VOS) : Ferry, MV

High frequent, high density observation
Temporal Marine Pollution

Heavy metal : Hg (Minamata disease) etc.

Nutrient : Red tide

Oil : Oil spill accident, bilge

Organic pollutants : Chemicals, Organic-thin, PCB
Endocrine Disrupter
POPs Treaty

Stockholm Treaty about Persistent Organic Pollutants

May, 2001, Stockholm

POPs
① Persistence
② Bioaccumulation
③ Potential for long-range environmental transport
④ Toxicity (or adverse effects)
12 Chemicals

Aldrin (insecticide), Dieldrin (insecticide), Endrin (insecticide),
Chlordane (insecticide), Heptachlor (insecticide),
Mirex (fire prevention), HCB (insecticide),

**PCB** (isolation oil, heat medium), **DDT** (insecticide),

PCDDs, PCDFs
Which path pollutants transport to the sea?

- Air
- Land (Chemicals, Industrial wastewaters, House wastewaters, etc.)
- River
- Ship (Paint, bilge)

Dissolve, dumping
Ocean: Need Observation Vessels

Earth

Water Ball

Lack of Observation Vessels
Various contaminants

Impact versus difficulty of Measurement for contaminants/analytes

GOOS

- **Category 1**
  - Nutrients
  - DO, SPM, Phytoplankton Pigments
  - plastics
  - Oil

- **Category 2**
  - Artificial radionuclides
  - Pharmaceuticals

- **Category 3**
  - Synthetic Orgs.
  - Herbicides/pesticides
  - PAHs

**GOOS**

The Global Ocean Observing System

Prospectus 1998

UNESCO
Lack of observation data

- Costal zone: 1 data/y (EA Annual Report: Environment and Chemicals)
- The Ocean: 1 data/10 – 20 y

HCHs in air and surface water (all data from 1980 to 1995)
Almost pollutants are very low concentration

If pollutants are very low concentration, can’t be relieved, because pollutants are concentrated high level with food web.

If pollutants can not detect, is not no-existence. We can’t detect now by present methods.

Colborn et. al.  
From Our Stolen Future
One of solution for lack of observation vessels

Ferry use for observation platform(vessel)
Ferry “Kurosio” : Osaka—Naha
Concentrating sampling system

Flowmeter

Prefilter

Concentrating column
Concentrating sampling system (homemade)
Procedure: Seawater 100L $\rightarrow$ 0.1mL : Concentrated rate 1,000,000

- Seawater 50~100L
- Solid state extraction
- Acetone 24hr
- Soxlet
- Concentrater
- Dehydration
- Hexane
- Concentrate
- GC-MS/SIM

0.1mL

10 mL
Results: $\beta$-HCH between Osaka and Naha
Ferry “Sunflower Ivory” : Osaka—Beppu
Concentrating sampling system (homemade)

- electronic signals
- sea water pipes

inlet
pump
filter
flow meter
FC valves
drain
controllers
electric valves
concentrating columns

GPS信号
ノートパソコン
3rd generation system (homemade)
Results: HCHs between Osaka and Beppu

September, 1999
Airsampler: sampling of chemicals in the air
Airsampler: PUF sampler
Chemicals detected all sampling points, but they were very low Concentration (10 ~ 1000 ppq).

\[ 1 \text{ppq} = 10^{-15} \quad 10 \text{ppq} = 10^{-14} \]

40f container: 8f x 8f x 40f \( \div \) 70m\(^3\) = 70,000L

\[ \frac{1 \text{g}}{10^{14} \text{mL}} = \frac{1 \text{g}}{10^{11} \text{L}} \]

\[ \frac{10^{11} \text{L}}{70000 \text{L}} \div 1.4 \times 10^6 \]

1,400,000 40f containers

\[ \frac{1,400,000}{3250} \div 430.8 \text{ (NYK ATLAS)} \]
Observation results: t-chlordane
Observation results: Chlordanes in the air
High frequency and high density observation using MV should be very powerful method for analysis of movements of pollutants in marine environment.
Figure 2.2. Schematic representation of the global fractionation hypothesis and the revolatilization (●) or ‘grasshopper’ effect. From Wania and Mackay (1996).
Next step: What powerful tools we have?

Use of MV for observation platform, condensation sampling and high-sensitive analytical system

This total system must be very attractive and powerful methods for monitoring and analysis of marine pollutions

Key point: How to secure VOS-MV
Next Step: VOS-MV

Can we use MV for VOS with various routes and continuously?

Need support by a shipping agent

NYK operate over 400 ships;
70 Container ships, 25 VLCCs, LNGs,
60 Car carriers, etc.
Next step: Various routes
1st ship: VLCC “TAKASUZU”
New System

Control computer

Extracting sampling

Water sampling

sensors
Sampling system: Solid phase extracting

Column holder
Sampling points (Japan – Middle East)
200012-0102, 200210-200302
Observation result: TBT
Observation results: MBT

MBT: Decomposed from TBT

Lambert's azimuthal equal-area projection

往路 復路

2 ppt
Concentration distribution of Pb in surface seawater along the tanker track between Japan and Saudi Arabia.

●: Outward, ○: Homeward. ——: Literature value for surface seawater in East-China Sea


The concentrations of Pb in seawater were relatively high near Japan (right end of the figure), and then they became gradually lower in sea area far from Japan. They were relatively low and constant in sea area at 120 degree and westward. Since Pb are mainly discharged from cars, the high concentration of Pb in seawater would indicate the existence of a car society.
2nd ship: Coal carrier “Shinchi-maru”

58,000t
Observation Systems

Column Sampling Unit

Control and Senser Unit

Water Sampling Unit
Sampling points (200201-02, 200208-0302, 200401, 08)
Observation results: $\beta$-HCH between Japan and Australia
3rd Ship: Passenger boat “Asuka”

- Column Sampling Unit
- Senser Unit
Sampling points of Sinchimaru (2003/12/28-2004/1/9) and Asuka (2004/1/20-2/22)
Simultaneous multi-component multi-element collecting system

Applicable for POPs measurement,
Added Activated Carbon Fiber adsorbents.
Internal standard
<table>
<thead>
<tr>
<th>化合物名</th>
<th>構造式</th>
<th>濃度 (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-HCH(1³C₆,99%)</td>
<td>¹³C₆H₆Cl₆</td>
<td>0.8</td>
</tr>
<tr>
<td>β-HCH(1³C₆,99%)</td>
<td>¹³C₆H₆Cl₆</td>
<td>0.8</td>
</tr>
<tr>
<td>γ-HCH(1³C₆,99%)</td>
<td>¹³C₆H₆Cl₆</td>
<td>0.8</td>
</tr>
<tr>
<td>trans-Chlordane(1³C₁₀,99%)</td>
<td>¹³C₁₀H₆Cl₈</td>
<td>0.8</td>
</tr>
<tr>
<td>trans-Nonachlor(1³C₁₀,99%)</td>
<td>¹³C₁₀H₅Cl₉</td>
<td>0.8</td>
</tr>
<tr>
<td>cis-Nonachlor(1³C₁₀,99%)</td>
<td>¹³C₁₀H₅Cl₉</td>
<td>0.8</td>
</tr>
<tr>
<td>4,4'-DDT(ring-1³C₁₂,99%)</td>
<td>(Cl¹³C₆H₄)₂CHCCl₃</td>
<td>0.8</td>
</tr>
<tr>
<td>4,4'-DDD(ring-D₈,99%)</td>
<td>C₁₄D₈H₂Cl₄</td>
<td>0.8</td>
</tr>
<tr>
<td>4,4'-DDE(ring-1³C₁₂,99%)</td>
<td>(Cl¹³C₆H₄)₂CHCCl₃</td>
<td>0.8</td>
</tr>
<tr>
<td>Aldrin(1³C₁₂,99%)</td>
<td>¹³C₁₂H₈Cl₆</td>
<td>0.8</td>
</tr>
<tr>
<td>Dieldrin(1³C₁₂,99%)</td>
<td>¹³C₁₂H₈Cl₆O</td>
<td>0.8</td>
</tr>
<tr>
<td>Endrin(1³C₁₂,99%)</td>
<td>¹³C₁₂H₈Cl₆O</td>
<td>0.8</td>
</tr>
<tr>
<td>Heptachlor(1³C₁₀,99%)</td>
<td>¹³C₁₀H₅Cl₇</td>
<td>0.8</td>
</tr>
<tr>
<td>Heptachlor Epoxide(1³C₁₀,99%)</td>
<td>¹³C₁₀H₅Cl₇O</td>
<td>0.8</td>
</tr>
<tr>
<td>Solvent</td>
<td>Nonane (n-Nonane)</td>
<td></td>
</tr>
</tbody>
</table>
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“Monitoring and Long-and Short-term Dynamics in the North-west Pacific Area”

• About 300 programs was selected by the Ministry of Education, etc. Japan
• 20 members, from various fields of science,
• Key: How do we preserve and make good use of the environment and ecosystem of the area of North-west Pacific Region Sea
Environmental Monitoring and Prediction of Long- & Short-Term Dynamics of Pan-Japan Sea Area

Commencement of the COE Program
Outline of the Project
Members
Young Researchers Support Program
Workshops & Conferences
Strategy of the Research
Links

News

- August 23, 2005 (Tuesday)  What’s New
  The second COE English class starts.

- July 26, 2005  What’s New
  Prof. Muramoto was commended.
  Distinguished services were commended. Please see Japanese news in details.

Symposium

- June 9-15, 2006  What’s New
  Joint International Meeting
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Monitoring chemical substances in Northwest Pacific Region Sea

- Necessity for the accumulation of data and “samples” of chemical substances in North-west Pacific Region Sea for preservation and make good use of it.
- Method developed by Dr. Kunugi (NIES, Japan) will be used.
- POI, FEFRAS kindly agreed to collaborate, load concentrating sampling machine to their scientific vessels.
Monitoring chemical substances in Northwest Pacific Region Sea

- Expertise is necessary for extraction, especially for detecting chemicals of very low concentration.
Thanks for attention.