

D-2.1.1 Clarification of Origin and Behavior of Marine Pollutants

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Abstract

To clarify emission sources of marine pollutants and their behavior, figure printing methods using lead isotope ratio or isomeric pattern of organochlorine compounds were developed. Lead concentration and isotope ratio were determined for coastal seawater samples and open ocean seawater samples, collected during the cruise of the Hakurei-Maru from August to September. Samples from Sendai Port, Chiba New Port, Tokyo Bay St. 22 and Tsushima Omodahama have different isotopic data compared with those for the open ocean seawater samples. It suggests that the lead in the coastal seawater samples has different origins and is thought to be influenced by industrial activities. Isomer specific analysis of PCN (polychlorinated naphthalene) was performed for several fly ash samples taken from incinerators and sediment samples in an industrial area to clarify the behavior of PCN. The isomer patterns turned out to be specific to each emission source. The major source of PCN in the industrial area was regarded to be technical products. The isomer patterns have changed from those of the sources because of biodegradation. The degradability seemed to be higher for the isomers such as 1,4,5-trichloro-naphthalene, 1,4,5,8- and 1,2,4,8-tetrachloronaphthalene which had many peri-substituted Cl atoms compared with other isomers. Preconcentration method using XAD-2 resin was also developed for the trace levels of organotin compounds in seawater.

Key Words Marine pollution, Emission Source, Lead, Chlorinated Organic Compounds, Finger Print Method

1. Introduction

Marine pollution due to hazardous wastes and chemical substances is now a globally important problem. These substances are liable to be accumulated in marine ecosystem and finally cause a serious effect to human life. It is important, therefore, to determine toxic substances in sea water, etc. and to clarify their emission sources and the behavior. To elucidate the problem, the present study focused on the behavior of marine pollutants such as organotin compounds, lead and chlorinated organic compounds, and the discrimination method of emission sources of these substances.

2. Results and Discussion

(1) Preconcentration of organotin compounds in seawater with XAD-2 resin

Tributyltin chloride (TBTC) and triphenyltin chloride (TPTC), used as antifouling paints for shipbottoms, cause serious environmental pollution. Due to the very low (sub-ppb) concentrations of these compounds in seawater, preconcentration procedures are necessary for their precise determination. By using Amberlite XAD-2 resin, TBTC and TPTC added to artificial seawater, they were found to be completely adsorbed into the resin. The

preconcentration procedure developed in this study is shown in Fig. 1. The organotin compounds collected in XAD-2 column were eluted with 10 ml of ethanol at first, and then, with hexane-ethanol mixture ($v : v = 1 : 1$). The first elution with ethanol was effective in removing the moisture remaining inside the resin. With this procedure, TBTC and TPTC were recovered with an efficiency of more than 95%. After preconcentration, these organotins were converted into their hydrides with sodium borohydride and determined by gas chromatography with a flame photometric detector. The detection limits for TBTC and TPTC were 0.04 ng and 0.10 ng, respectively. The advantage of this method is to enable the on-site preconcentration of organotins, for example,

(2) Determination of lead isotope ratios and concentrations in seawater by ICP-MS

The concentration of lead in seawater is increasing owing to industrial activity and gasoline combustion.¹⁾ To solve the problem of lead pollution of seawater, it is important to clarify the origin of the lead present by measuring the lead isotope ratios.²⁾ Hitherto, thermal ionization mass spectrometry (TIMS) has been used for this purpose. Although it allows the isotope ratios and concentrations to be determined very accurately and precisely, it is time consuming. A faster method would be advantageous for environmental studies where many samples have to be analysed. Inductively coupled plasma mass spectrometry (ICP-MS) seems to be the best alternative method. As the lead concentration in open seawater is below several tens of ng/l and seawater contains large amounts of salts, some preconcentration and matrix separation procedure is essential in order to determine accurately the isotope ratio and concentrations of lead.

(i) Materials and Methods

Seawater samples: Coastal seawater samples were taken from the surface of the sea with a pre-cleaned polyethylene beaker connected to a nylon rope and stored in an acid-washed 10 l polyethylene tank. Open ocean seawater samples were likewise collected during the cruise of the Hakurei-Marui, Japan, from August to September, 1991.

Preconcentration procedure: To avoid contamination, the column system for preconcentration was designed to be closed from the atmosphere. After cleaning the resin with 5 M HCl, water and 2M HNO₃, the resin (2.5 g) was packed into the column and preconditioned with ammonia solution, water and ammonium acetate buffer (pH 6) prior to each use. A 1 l seawater sample was filtered through a 0.45 μ m Millipore filter and 10 ml of 1M ammonium acetate buffer solution was added. The pH was adjusted to pH 6 with 2M ammonia solution and 1M acetic acid. The solution was passed through the Chelex-100 column using a peristaltic pump at a flow rate of 2.0 ml/min. The resin was then washed with 50 ml of water and for removal of matrix salts the column was treated with 80 ml of 1M ammonium acetate

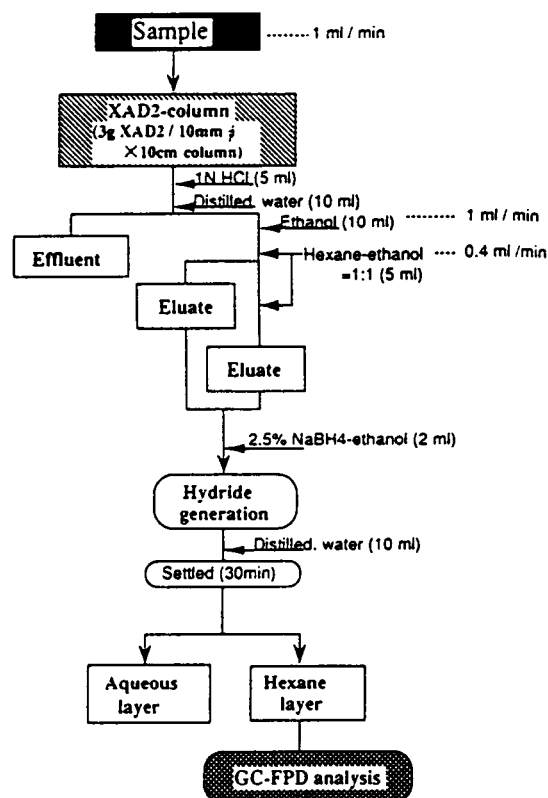


Fig. 1 Preconcentration procedure for organotin compounds

buffer and 80 ml of water after each seawater pre-concentration. The trace metal pre-concentrated on the resin was eluted with 10 ml of 5M HNO₃ followed by 10 ml of water into a PTFE beaker. Then, 6 ml of concentrated HCl were added and the sample was evaporated to dryness on a hot-plate in a flow of clean air. Residual ammonium nitrate was volatilized in this step. The residue was dissolved in 5 ml of 0.2M HNO₃, placed in a 10 ml calibrated flask and diluted to volume with water. The 100-fold concentrated solution was diluted 10-fold in order to minimize the salt content and was then ready for ICP-MS measurement. All procedure were carried out on a clean bench or in a laminar flow cabinet.

(ii) Results and Discussion

Isotope ratio: The isotope ratio of lead varies because of the radioactive decay of ²³⁸U to ²⁰⁶Pb, ²³⁵U to ²⁰⁷Pb and ²³²Th to ²⁰⁸Pb. One isotope, ²⁰⁴Pb, has no long-lived radioactive parents. Hence differences in the isotopes of lead arise primarily from differences in the ages and parent : daughter ratios in the geochemical formations. These differences are reflected in oceanic waters, which receive lead input from geochemical formations via weathering processes. Therefore, the measurement of isotope ratios of lead in seawater is useful when considering the origin of the lead.

To confirm the accuracy of isotopic data, NRCC NASS-3 Open Ocean Seawater and NIST SRM 981 were analysed. Our results were in good agreement with those obtained in other work or with the certified value. The standard deviations in this work were based on sub-samples carried through the procedure. Isotope data are plotted in Fig. 2 for coastal seawater and open ocean seawater samples. As can be seen from Fig. 2, the data for Chiba New Port, Tsushima

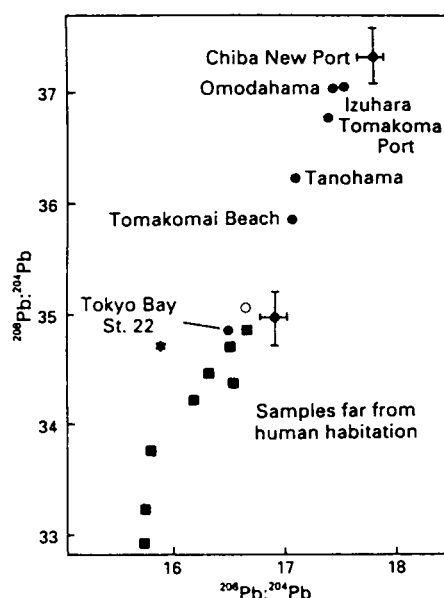


Fig. 2 Isotope ratio for coastal sea-water: ● and ■ sea-water sample; ○, NASS-3; and ★, SRM 981. The bars in the figure indicate the standard deviation of the data

Table 1 Analytical results for sea-water samples

Sample	Pb concentration/ $\mu\text{g l}^{-1}$	Sample	Pb concentration/ $\mu\text{g l}^{-1}$
<i>Open Ocean*</i> —		<i>Coastal sea-water</i> —	
48°N 175°E	0.046	Okinawa	
44°N 175°E	0.044	Naha, Tomari Port	0.131
38°N 175°E	0.040	Naha, Tomari Port	0.097
30°N 175°E	0.043	Naha, near Tomari Port	0.061
27°N 175°E	0.044	Awazure Hama	0.050
8°N 175°E	0.040	Motobu, Bize Cape	0.070
0°N 175°E	0.043	Motobu, Bize Cape	0.043
<i>Coastal sea-water</i>		Henoko Cape	0.054
Sendai		Hokkaido	
Sendai Port	0.087	Tomakomai Port	0.300
Tokyo Bay		Tomakomai Beach	0.200
Chiba New Port, 17 m depth	0.203	Tsushima	
St. 22, 22 m depth	0.167	Omodahama	0.111
		Izuhara Port	0.130
		Tanohama	0.080
		Miutahama	0.078

*Pacific Ocean.

Omodahama, Tsushima Izuhara, Tomokomai Port, Tsushima Tanohama and Tomakomai Beach are apparently different from those for the other samples. This result suggests that the lead in the coastal seawater has different origins from those for the other samples and is thought to be influenced by industrial activities. Although further measurements of lead isotopes are necessary to elucidate the origin of the lead in seawater samples, the above results demonstrate that ICP-MS is useful for the measurement of variations in lead isotope ratios not only in the coastal seawater samples but also open ocean water samples.

Concentration: The lead concentrations in open ocean and coastal seawater samples are summarized in Table 1. The concentrations were measured using the external calibration graph method with simple acid standards. The ICP-MS method gave simultaneously four concentrations which were measured at four masses. As the four values agreed within an error of 0.8%, the concentrations given in Table 1 are the values measured at m/z 208. The lead concentration in open ocean seawater was found to be low than that in coastal seawater. The results demonstrate that the preconcentration method using a chelating resin combined with ICP-MS is useful for the determination of lead in seawater.

(3) Isomeric patterns of chlorinated organic compounds

Some of the isomers of polychlorinated naphthalenes (PCNs) are known to be strongly bioaccumulating and showing "dioxin-like" activities. Toxic equivalence factors were reported for some of the isomers. Recently, Auger et al. synthesized and characterized several important isomers including strongly bioaccumulating 1,2,3,4,6,7-/1,2,3,5,6,7-hexachloronaphthalenes(HxCNs). Williams et al. detected 1,2,3,4,6,7- and 1,2,3,5,6,7-HxCNs in human adipose tissue together with one HxCN and one pentachloronaphthalene (PnCN) isomer with unknown structure. However, many isomers remain unidentified especially PeCNs and tetrachloronaphthalenes(TeCNs).

In this study, unknown isomers of HxCNs, PnCNs and TeCNs were identified on gas chromatograms of Halowax and fly ash extract.

(i) Materials and Methods

Synthesis of PCN isomers: Synthetic methods for TeCN are reported only for several isomers. So we synthesized the majority of TeCN isomers by chlorine substitution reactions of naphthalene derivatives of known structure. The substituent groups replaceable by Chlorine in the reaction with phosphorous pentachloride are; -OH, -SO₃H, -NO₂, -N₂R and =O. For example, 1,2,3,6-TeCN was obtained by heating 1-(4-nitrophenyl) diazo-2-naphthol-3,6-disulfonic acid disodium salt (Tokyo Kasei Chem.,G.R.) with PCl₅. Higher chlorinated by-products were found together with the intended isomer. PnCNs formed by this reaction were used for identification in case their structures were confined according to the starting materials.

For HxCN, six isomers were already identified. To identify the rest, 1,2,3,4,5,8-, 1,2,3,5,6,8- and 1,2,3,4,5,7-HxCN isomers were synthesized. 1,2,3,4,5,8-HxCN was obtained by heating 2,3-dichloro-5,8-dihydroxy-1,4-naphthoquinone(Aldrich) with PCl₅. 1,2,3,5,6,8-HxCN was obtained from 1,2,3,6-tetrachloro-5,8-naphthoquinone derived from the oxidation of 1,2,3,6-TeCN. 1,2,3,4,5,7-HxCN was obtained from the chlorination of 1,2,3,4-TeCN(Aldrich) by surfuryl chloride together with three HxCN isomers.

Extraction and clean-up methods for fly ash: Air-dried fly ash (20g) collected from a municipal incinerator was digested with hydrochloric acid and was Soxhlet extracted with toluene for 24 h. The extract dissolved in n-hexane was washed by aqueous sodium hydroxide and sulfuric acid. After removal of sulfur by activated copper, it was purified by silica gel and alumina column.

Gas chromatography/ mass spectrometry: For the synthesized PCNs, m/z up to 600 were scanned in 2 sec to obtain full mass spectra by a GC/MS, Hitachi M-80B.PCNs in Halowax

and fly ash were analyzed in selected ion monitoring (SIM) mode. The operating conditions are summarized in Table 2.

(ii) Results and Discussion

Fifteen isomers among twenty-two TeCN isomers were obtained from tetra-substituted naphthalene derivatives. These isomers are; 1,2,3,4-, 1,2,3,6-, 1,2,4,5-, 1,2,4,6-, 1,2,4,7-, 1,2,4,8-, 1,2,5,6-, 1,2,5,8-, 1,2,6,8-, 1,2,7,8-, 1,3,5,7-, 1,3,6,7-, 1,3,6,8-, 1,4,5,8- and 2,3,6,7-TeCN. 1,2,3,5-, 1,3,5,8- and 1,4,6,7-TeCN were synthesized via hexachlorotetraline. Four isomers (1,2,6,7-, 1,2,5,7-, 1,2,3,7-, 1,2,3,8-) remained unidentified and were obtained from photodecomposition of 1,2,3,6,7-, 1,2,4,5,7-, 1,2,3,4,6-, 1,2,3,4,5-PnCN, respectively.

Among fourteen PnCN isomers, 1,2,3,6,7- and 1,2,4,5,8-PnCN isomers were identified because no other PnCNs can be the by-products of 2,3,6,7- and 1,4,5,8-TeCN, respectively. The following isomers were identified because they were obtained by duplicating by-products from different starting materials; 1,2,3,4,5-, 1,2,3,4,6-, 1,2,3,5,6-, 1,2,3,5,7-, 1,2,3,6,8-, 1,2,3,7,8-, 1,2,4,5,6-, 1,2,4,5,7-, 1,2,4,6,7-, 1,2,4,6,8- and

Table 2 Operating conditions of GC/MS for PCN analysis

GC	Column: OV-1701, 0.25mm, 25m Temp.: 140 - 280 °C, 6°C/min Carrier: He 69kPa
MS	EI 70eV, Ion source: 180°C Selected ion monitoring m/z Tetrachloronaphthalene 264,266 Pentachloronaphthalene 300,302 Hexachloronaphthalene 334,336 Heptachloronaphthalene 368,370

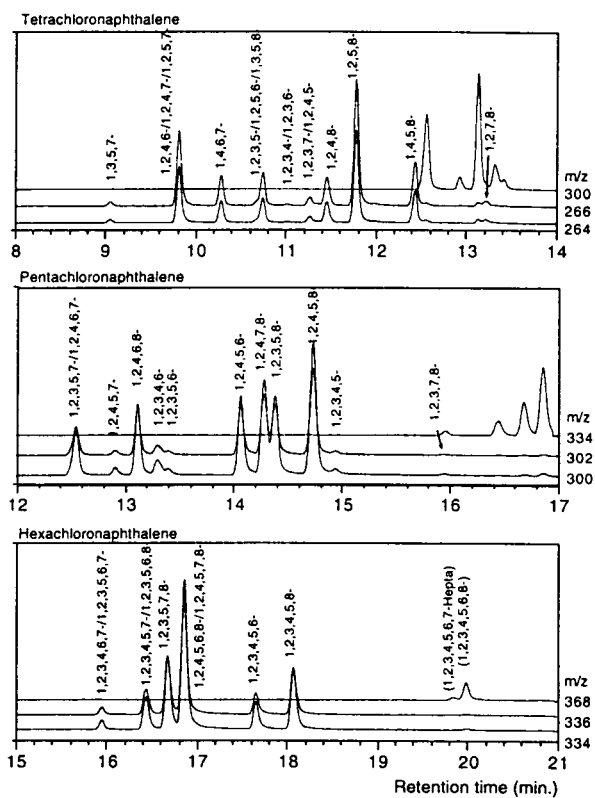


Fig.3 Chromatograms of PCNs in Halowax 1014

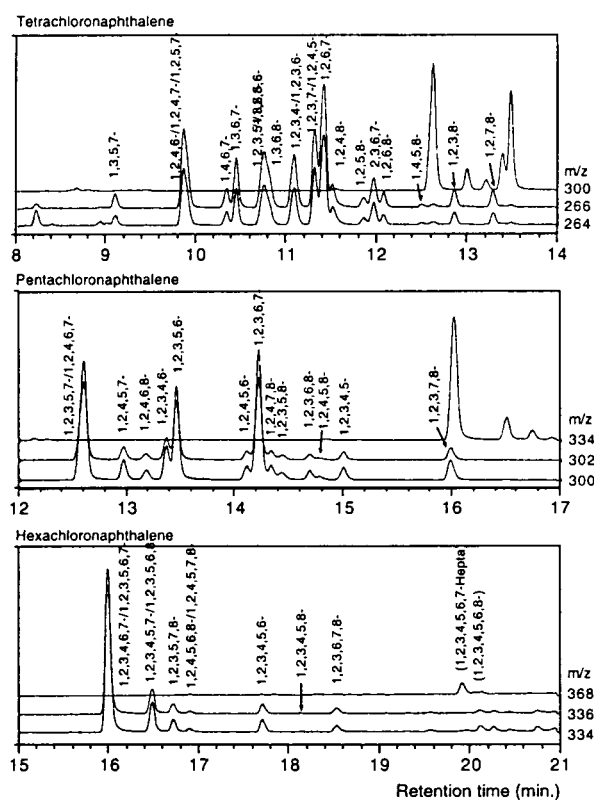


Fig.4-Chromatograms of PCNs in fly ash from an incinerator

1,2,4,7,8-. One peak remained unknown on SIM chromatogram was identified as 1,2,3,5,8-PnCN.

Among ten HxCN isomers, chromatographic data for identification were reported for 1,2,3,4,6,7-, 1,2,3,5,6,7-, 1,2,4,5,6,8-, 1,2,4,5,7,8-, 1,2,3,4,5,6- and 1,2,3,6,7,8-. Three unknown peaks on GC chromatogram remained for four unidentified isomers. 1,2,3,4,5,8- and 1,2,3,5,6,8-HxCN corresponded to two unknown peaks. The chlorination product of 1,2,3,4-TeCN gave three peaks corresponding to 1,2,3,4,6,7-, 1,2,3,4,5,6- and 1,2,3,4,5,8-HxCN, and one peak at the same retention time with 1,2,3,5,6,8-HxCN. We concluded 1,2,3,4,5,7-HxCN is overlapping with 1,2,3,5,6,8-HxCN and the only one remaining peak must be 1,2,3,5,7,8-HxCN. Confirmation by different method is necessary for these isomers.

Isomers of TeCNs, PnCNs and HxCNs found in Halowax 1014 were assigned as shown in Fig.3.

Some of the isomers such as 1,2,6,7-TeCN, 1,2,3,6,7-, 1,2,3,6,8-PnCN or 1,2,3,6,7,8-HxCN were not found in Halowax.

In municipal incinerator fly ash, all isomers were found and they were assigned as shown in Fig.4. In this sample, 1,2,3,4,6,7-/1,2,3,5,6,7-HxCNs were dominating HxCN. Stoker type incinerators tend to give a similar isomer pattern to Fig.4. Concentration of PCNs was at the same level as that of PCDDs.

The isomer pattern of PCNs from waste incineration was thus entirely different from that of technical PCNs. From this property, discrimination of the sources of PCNs found in environmental sample is possible. PCNs found in the sediment samples near industrialized area gave the isomer patterns resembling to that of technical PCNs except for the low occupation of 1,4,5- TrCN, 1,2,5,8-TeCN, 1,4,5,8-TeCN and 1,2,4,5,8-PnCN. This phenomenon can be explained that these isomers are easier to decompose in environment. This fact also indicates that biodegradation should be taken into consideration in the pattern recognition method.

References

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