

## OCCURRENCE OF 888 CHEMICALS IN SEDIMENTS IN AN ENCLOSED BAY IN KITAKYUSHU, JAPAN

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### Abstract

Sediments of an enclosed bay in Kitakyushu, Japan, which was shown by past surveys to be polluted with complex mixtures of organic chemicals, were tested for 888 chemicals by a newly developed comprehensive analytical method. The results of analysis of a standard reference material, NIST 1941a, showed that determination ability of the new method was close to that of conventional internal-standard methods, even though standard substances were not used. Of the 888 chemicals, 192 were found in the sediments, and their concentrations increased closer to the innermost of the bay. The chemicals with the highest concentrations were 16 polycyclic aromatic hydrocarbons (PAHs), classified by the US EPA as priority pollutants, and their concentrations were the same as had been determined in the past, despite their suspected emission sources being eliminated in 1997, indicating that PAHs are not easily decomposed in anaerobic sediments. Comparison of the PAH concentrations with sediment quality guidelines indicated that the sampling sites from the center to the innermost of the bay were of Level 2 concern, coinciding with the part of the bay showing a low diversity of benthic animals, according to a biological survey.

### Introduction

Pollution by chemicals of environmental waters in Japan has been lessened by the implementation of various regulations. However, marine sediment quality has not improved because of the slow decomposition of chemicals that were discharged and accumulated in sediments in the past. Therefore, because these sediments can become a secondary source of water pollution, with adverse effects on both the resident benthos and the aquatic ecosystem generally, a survey of the sediments is needed. We have developed a novel GC-MS database<sup>1</sup> and have been developing comprehensive analytical methods that utilize the database for various environmental media. The objectives of the present study were to (1) evaluate the performance of the developed comprehensive analytical method for sediments and (2) investigate pollution by 888 chemicals of sediments in Dokai Bay, an enclosed bay in Kitakyushu, Japan. This bay was called the “Sea of Death” in the 1960s, but since then the water quality has improved and more than 100 species of aquatic animals have returned<sup>2</sup>. However, it is known that the bay’s sediments are still polluted with complex mixtures of organic chemicals from past surveys.

### Materials and Methods

#### Study area

Dokai Bay, in Kitakyushu City, Japan (Fig. 1), is a typical enclosed bay: 13 km long and 300 m wide at its narrowest point, and 10 m deep at its deepest point. Many factories, including steel and chemical factories are located around the bay; the biggest emission source is located near Stn.6. Four small rivers and effluent from a sewage treatment plant flow into the innermost part of the bay near Stn 7.

#### Samples

Sediment samples were collected from seven sites (Fig. 1) with an Eckman-Barge grab sampler (15 × 15 cm) on 26 January 2007. The surface sediment layer, to a depth of 5 cm, was used for the chemical analyses.

#### Analytical method

Each sediment sample (20 g, wet) was extracted 3 times with 30 ml of acetone. Then, the extracted fluid was concentrated to 10 ml with a rotary evaporator, and the concentrate was added to 200 ml of salt water. Then, the water mixture was extracted twice with 20 ml of dichloromethane. After dehydration of the extract, 20 ml of

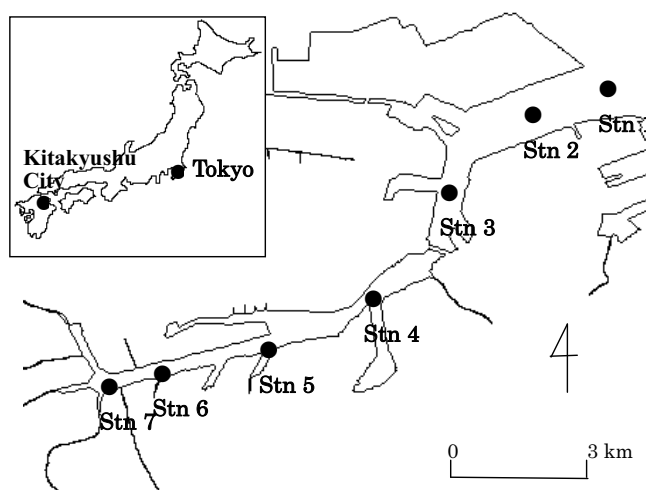


Fig. 1 Sampling locations

hexane was added, and the mixture was concentrated to 5 ml with a rotary evaporator. One milliliter of the concentrate was applied to a silica-gel cartridge (Waters VAC 12 cc) and fractionated into 3 fractions (hexane, 5% acetone-hexane, and 30% acetone-hexane, each 15 ml). Each fraction was concentrated to 1 ml with a rotary evaporator and measured by GC-MS after the addition of internal standards. GC-MS conditions were as reported previously<sup>1</sup>.

For quality control, we analyzed a blank sample and performed a duplicate analysis and analysis of a standard reference material (NIST 1941a). Since the comprehensive analytical method uses a database system instead of analyses of standard solutions of target chemicals to identify and quantify chemicals, it is less expensive and requires less time than analyses using conventional methods. But because the method has been applied to few data, its quantification ability, precision, and accuracy have not been fully recognized. Thus, to evaluate the quantification ability of the new method, we analyzed a certified marine sediment sample (NIST 1941a) using the same procedures.

## Results and Discussion

### Analytical results of NIST 1941a

In NIST 1941a, although concentrations of 67 substances which include both certificated and noncertified values are shown, 57 substances were able to be detected. The mean ratio of detected to certified values was 1.06, and the relative standard deviation of the ratios was 0.52. Most of ratios were between 0.5 and 2.0, indicating that the accuracy of the comprehensive method, although lower than that of the conventional internal-standard method, is sufficient for environmental survey. However, chemicals at concentrations below 10 µg/kg were not identified automatically by the database software, and their detected values differed greatly from the certified values. *n*-Alkanes, which were also found in the blank at relatively high concentration, and chemicals with a low boiling point were also not correctly quantified. The concentration steps by rotary evaporation was a cause of low recovery of low-boiling-point chemicals. These results confirmed that for sediments having a large amount of matrix, most chemicals, except for those at concentrations near the instrument detection limit, could be automatically identified and correctly quantified.

### Outline of survey results

Chemical groups at each site were categorized by use or origin (Table 1). Although a total of 192 substances were found, the number of detected chemicals increased toward the innermost of the bay. Characteristically, the detected substances were intermediate products of chemical synthesis and other chemical products, such as aromatic amines, nitro compounds, chlorobenzenes, and chlorophenols. Although polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in the environment, their concentrations were extremely high, particularly near the innermost of the bay. Thus, these characteristic chemicals were apparently discharged from factories located around the bay. Since the other chemicals detected are also ubiquitous in the environment, they apparently were transported into the bay by rivers as well as discharged by the sewage treatment plant and factories. Total concentration of all substances showed a trend similar to that of a number of the detected chemicals: Stn 6 had the highest total concentration, 247 mg/kg dry, which was about 28 times that at Stn 1, at the mouth of the bay. Although organic carbon at Stn 6 was 17.4%, 4 times its value at Stn 1 (4.3%), the organic carbon-based concentration at Stn 6 was 7 times that at Stn 1. In particular, the concentration of PAHs was highest at Stn 6, where it was 76 times that at Stn 1 (Fig. 2). Jinya et al. investigated the behavior of organic chemicals in the water column in Dokai Bay and reported that highly hydrophobic chemicals such as PAHs were easily absorbed onto suspended solids, which settle onto the sea bottom near emission sources<sup>3</sup>. The profile of PAH concentrations obtained in the present study is consistent with that finding.

### POPs concentrations

Among persistent organic pollutants (except PCDDs, PCDFs, mirex, and toxaphene, which are not registered in the database), PCBs were detected at 6 sites (except for Stn 1), whereas HCB and DDTs were detected only at Stn 6 and Stn 7. Since the DDT concentration at Stn 7 was higher than at Stn 6, DDTs apparently were transported into the bay by rivers. The higher concentration of HCB at Stn 6 suggests that its sources were factories. PCB concentrations showed 2 peaks, suggesting that there were many sources of PCBs.

### Differences in contamination levels among sampling sites

Chemicals were separated into two groups by the spatial distribution of their concentrations; the first group, including the PAHs, had a maximum concentration at Stn 6 (Fig. 2), and concentrations of the second group peaked at Stn 7. Since river water and effluent from a sewage treatment plant flow into the innermost of the bay near Stn 7, these were apparently the sources of the chemicals in the second group. In fact, the second group consisted of chemicals discharged from households and paddy fields, such as pesticides, sterols, antioxidants,

Table 1 Concentrations ( $\mu\text{g}/\text{kg}$  dry) of chemical groups at each site classified by use or origin

Category	Stn 1	Stn 2	Stn 3	Stn 4	Stn 5	Stn 6	Stn 7
Insecticides (159)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	74 (3)	113 (2)
Herbicides (108)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	7 (1)	72 (4)
Fungicides (96)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	366 (1)	234 (1)
Other pesticides (35)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	16 (1)
Sterols (7)	2,233 (5)	1,939 (4)	10,019 (5)	11,357 (4)	9,039 (5)	14,146 (5)	14,620 (5)
Antioxidants (6)	1,685 (2)	3,389 (3)	5,156 (3)	7,032 (3)	5,251 (3)	4,303 (3)	6,048 (3)
Fragrances and cosmetics (11)	49 (5)	78 (4)	933 (6)	1,007 (5)	692 (5)	1,644 (4)	1,443 (4)
Disinfectants and insecticidal fumigants (4)	2 (2)	4 (2)	11 (3)	55 (3)	96 (4)	229 (4)	260 (4)
Fatty acid methyl esters (36)	16 (5)	51 (5)	13 (3)	113 (4)	53 (4)	79 (2)	103 (2)
Fire retardants (13)	108 (1)	0 (0)	10 (1)	41 (2)	21 (2)	75 (2)	162 (3)
Plasticizers (14)	539 (6)	1,049 (7)	1,966 (6)	2,824 (6)	2,477 (7)	6,772 (6)	10,245 (7)
Metabolites of detergents (3)	53 (2)	163 (2)	391 (2)	252 (2)	203 (2)	676 (2)	1,201 (2)
PPCPs (18)	5 (2)	8 (2)	79 (3)	154 (3)	110 (3)	447 (2)	1,641 (3)
Leaching compounds from tires (28)	74 (6)	178 (6)	484 (8)	703 (8)	816 (7)	1,746 (7)	2,224 (11)
Petroleum (26)	1,221 (24)	1,826 (23)	5,892 (24)	9,035 (25)	7,927 (25)	30,092 (25)	37,549 (25)
Other substances of domestic origin (29)	0 (0)	0 (0)	0 (0)	14 (1)	13 (1)	69 (5)	66 (3)
Intermediates in organic synthesis (59)	56 (6)	150 (7)	857 (9)	1,539 (13)	2,556 (13)	6,152 (15)	5,076 (16)
Intermediates for dye (26)	18 (1)	45 (1)	521 (1)	1,168 (1)	1,004 (4)	2,083 (7)	1,558 (7)
Intermediates for pesticide (6)	0 (0)	0 (0)	0 (0)	0 (0)	3 (1)	33 (1)	32 (1)
Intermediates for resin (8)	0 (0)	2 (1)	4 (1)	14 (2)	13 (2)	50 (2)	58 (1)
Solvents (17)	19 (5)	57 (5)	428 (6)	388 (8)	168 (7)	623 (8)	569 (7)
PAHs (46)	2,338 (30)	5,115 (32)	41,436 (32)	77,492 (32)	83,112 (31)	176,860 (33)	110,028 (34)
PCBs and PCNs (90)	0 (0)	3 (1)	340 (15)	167 (10)	81 (7)	360 (13)	134 (5)
Explosives (6)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)
Other substances of industrial origin (37)	340 (3)	168 (4)	592 (3)	501 (3)	184 (3)	220 (3)	219 (3)
Total (888)	8,756 (105)	14,225 (109)	69,131 (131)	113,855 (135)	113,820 (135)	247,106 (154)	193,670 (154)

Parentheses show the number of chemicals.

and plasticizers (Table 1). On the other hand, chemicals in the first group, which comprised chemicals used as intermediates in organic synthesis and dye and solvent production, were discharged from factories located near Stn 6.

Target 888 chemicals were classified into 3 groups by their sources: agricultural, domestic (business/ household), or industrial. Figure 3 shows the contribution of these 3 sources at each site. The results confirmed that the sediments in the bay were strongly affected by factories, but those at the innermost of the bay were also affected by river water and effluent of a sewage treatment plant. Since it is known that it takes only 2 weeks for a complete exchange of seawater in the bay with outside seawater<sup>3</sup>, the effects of factories and rivers were weakened by dilution by outside seawater. As a result, both concentrations and the contribution of factories declined at sites nearer the mouth of the bay.

#### Evaluation of detected concentrations with sediment quality guidelines

To assess the effect of the detected chemicals on benthic organisms, we compared the concentrations to sediment quality guidelines published by the Wisconsin Department of Natural Resources<sup>4</sup>. Only total PAHs, whose concentrations were 0.14–0.47 of the probable effect concentration, at 5 sites (except for Stns 1 and 2) were categorized at Level 2: >Threshold Effect Concentration < Midpoint Effect Concentration. In fact, it has been reported that the diversity of benthic animals declines with proximity to the innermost part of the bay<sup>5</sup>. Since the less diverse areas coincide with those areas where high concentrations of PAHs were found, PAHs were deemed to be one of the causes of low benthic diversity. Additionally, despite their suspected emission sources being eliminated in 1997, their concentrations have not decreased, which was confirmed by comparison of concentrations in the present survey and the survey in 1999 (unpublished data). Their adverse effects therefore will most likely continue in the future.

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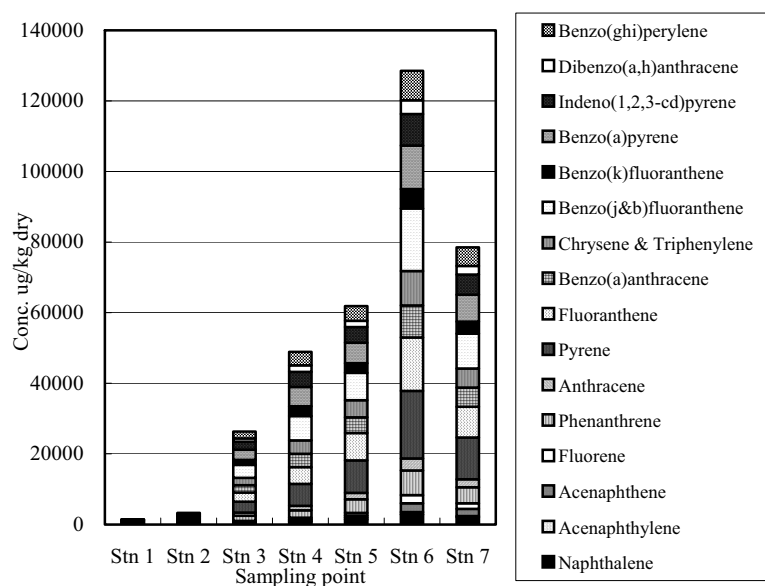


Fig. 2 PAHs concentrations at each site

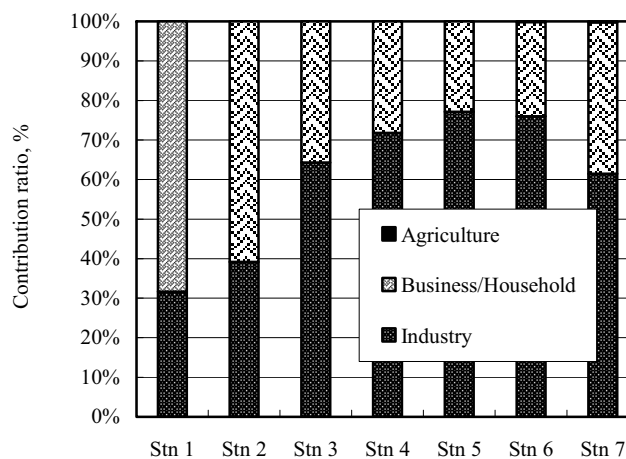


Fig. 3 Contribution of emission sources at each site