

Concentration and Characteristics of Polychlorinated Biphenyls in the Sediments of Sea and River in Nagasaki Prefecture, Japan

Takashi Honda,^{a,b} Mitsuhiro Wada,^a and Kenichiro Nakashima*,^a

^aGraduate School of Biomedical Sciences, Course of Pharmaceutical Sciences, Nagasaki University, 1–14 Bunkyo-machi, Nagasaki 852–8521, Japan and ^bNagasaki Prefectural Institute for Environmental Research and Public Health, 2–1306–11 Ikeda, Omura, Nagasaki 856–0026, Japan

(Received December 25, 2007; Accepted May 20, 2008; Published online May 26, 2008)

Environmental pollution with polychlorinated biphenyls (PCBs) continues in Japan due to their high persistency, although their manufacture and use have already been prohibited. In this study, PCBs in sediments at 67 sites in Nagasaki Prefecture were determined by GC-MS, and their profiles were compared with those of commercial PCBs (Kanechlor KC300-600). The concentrations of PCBs in the sediments of sea and river areas in Nagasaki Prefecture were found to be up to 2.5 and 0.035 µg/g, respectively. Higher concentrations of PCBs in the sediments of the sea compared to those from river were observed (except area D vs N). The profile of PCB homologues in the sediments of the sea areas was similar to that of Kanechlor KC600, whereas the profile of PCB homologues in the river sediments was similar to that of Kanechlor KC500. Moreover, the source contribution was estimated by a chemical mass balance (CMB) method using the composition ratio of major congeners of Kanechlor. As a result, it was found that the contributions of KC600 and KC500 were higher in sea sediments (ca. 60%) than in river sediments (ca 50%).

Key words — polychlorinated biphenyl, sediment, Nagasaki Prefecture, GC-MS, chemical mass balance method

INTRODUCTION

About 59000 t of polychlorinated biphenyls (PCBs) were manufactured from 1954 to 1972 in Japan, and about 54000 t were used within the country.¹⁾ PCBs have been widely used in heat exchange fluid, electric insulating oil for transformers and condensers, plasticizers, paint and carbonless copying paper. Such use is due to their remarkable characteristics such as chemical and thermal stability, acid-, alkali- and hydrolysis-resistance, water-insolubility, high electrical insulation, high boiling-point, and non-flammability.

However, its pollution has become one of the most serious environmental problems all over the world and many studies have been performed.^{2–5)} In Japan, the Kanemi-Yusho incident in 1968, which severely impaired human health, occurred by

contamination of cooking oil with PCBs.^{6–10)} Thereafter, PCBs were detected from various living organisms including humans and from environmental samples. As a result, the manufacture, import, and use of PCBs were prohibited in principle in 1974. However, environmental pollution with PCBs is still ubiquitous in Japan. The Ministry of the Environment in Japan has continuously analyzed PCBs in the sediments of water sources all over Japan.^{11–14)} Furthermore, many studies for determination of PCBs in sediments have been performed at various places in Japan such as Okinawa,¹⁵⁾ Sendai Bay,¹⁶⁾ Tokyo Bay,¹⁷⁾ Lake Suwa¹⁸⁾ and Ariake Sea.¹⁹⁾ To understand local pollution levels and the spatial distribution of PCBs, monitoring of PCBs in sediments is necessary. However, there is little available information to estimate PCB pollution in Nagasaki Prefecture.

Kanechlor, the major commercial PCB product used in Japan, has several types of products such as KC300, 400, 500 and 600 for a variety of purposes. KC300, containing primarily tri- and tetra-chlorinated congeners was used mainly in carbonless copying paper and in paper

*To whom correspondence should be addressed: Graduate School of Biomedical Sciences, Course of Pharmaceutical Sciences, Nagasaki University, 1–14 Bunkyo-machi, Nagasaki 852–8521, Japan. Tel.: +81-95-819-2450; Fax: +81-95-819-2450; E-mail: naka-ken@nagasaki-u.ac.jp

condensers. KC600, containing mostly hexa-through octa-chlorinated congeners was used in paint on the bottom of ships. These products have specific profiles of congeners and homologues²⁰⁾ and thus can contribute to the source of environmental pollution in Japan. KC300 corresponds to Aroclor (Ar) 1242, KC400 to Ar1248, KC500 to Ar1254 and KC600 to Ar1260 in terms of chlorine content.²¹⁾ Consequently, many studies used a profiling method of PCB homologues to detect the source of PCB pollution in Japan. On the other hand, a mathematical receptor model was required to recognize the source characteristics. For example, a chemical mass balance (CMB) method has widely been used for the source apportionment of organic pollutants in the environment. Imamoglu *et al.*²⁾ reported PCB contamination in lower Fox River sediments to identify the possible PCB sources. The CMB method confirmed that the PCB source was dominated by Ar1242 (average contribution 95%) with small amounts of Ar1254 (2%) and 1260 (1%).

The major objectives of this study were three-fold, as follows: to investigate local PCB concentration levels in the sediments sampled from 2000 to 2005 in Nagasaki Prefecture using a GC-MS method; to compare the profiles of PCB homologues in Kanechlor and the sediments and to evaluate the source contribution of PCB products by the CMB method²²⁾ for major congeners of Kanechlor. To our knowledge, this is the first report to evaluate the source contribution of PCBs in Nagasaki Prefecture by the CMB method.

MATERIALS AND METHODS

Chemicals — TPCB-CAL-A, TPCB-CL-A100 and TPCB-SY-A100 (Kanto Chemical Co., Tokyo, Japan) were used for calibration standard solutions, cleanup spikes and syringe spikes, respectively. TPCB-CAL-A consisted of 62 native congeners and 32 [¹³C]-labeled congeners of PCBs. TPCB-CL-A100 and TPCB-SY-A100 involved twenty-four types of [¹³C]-labeled congeners and seven [¹³C]-labeled congeners of PCBs respectively. Kanechlor standard solutions (KC300, KC400, KC500 and KC600) were purchased from GL Sciences (Tokyo, Japan). Toluene (Wako Pure Chemical Co., Osaka, Japan), hexane (Wako Pure Chemical Co.) and nonane (Wellington Lab., Guelph, Ontario, Canada) used were analysis grade for dioxin determination.

Sampling of the Sediments — Nagasaki Prefecture is located on the far west part of Japan, and has many isolated islands (*e.g.* I, J and K). Furthermore, Nagasaki Prefecture has various types of sea areas, such as bay or port areas and tidal flats (D). The locations of sampling sites at 67 sites are shown in Fig. 1. Sampling was performed in eleven sea areas (A to K) and six river areas (L to Q). The PCB concentrations in each water area are presented as a mean value from the sampling sites ($n = 1-8$). For a few river areas such as L, P and Q only one sampling site was used for each and PCB levels are those found at that site. The grab surface sediments from sea and river areas in Nagasaki Prefecture were sampled by an Ekman-Birge type bottom sampler (Miyamoto Riken Co., Osaka, Japan) in 2000–2005. Each sample was passed through a 2-mm mesh and freeze-dried for at least 24 hr in a freeze dryer (Taitec Co. Inc., Saitama, Japan). The water content was measured by drying at $105 \pm 5^\circ\text{C}$ for 2 hr and the ignition loss, a measure of organic matter content, was measured by heating at $600 \pm 25^\circ\text{C}$ for 2 hr. All data represent the concentration of PCBs on a dry-weight basis.

Pretreatment of the Sediments — PCBs in the sediments were extracted for at least 24 hr with 300 ml of toluene in a Soxhlet extractor equipped with a Dean-Stark trap and the extract was then exchanged into hexane, after concentration using a rotary evaporator. A glass multilayer silica gel column (Supelco Inc., St. Louis, MO, U.S.A.) was used for a pretreatment of Soxhlet extract solution. The following were packed in order from the top into a glass column (35 cm \times 15 mm, i.d.): 3 g of 10% AgNO₃/silica gel, 0.9 g of silica gel, 6 g of 22% H₂SO₄/silica gel, 4.5 g of 44% H₂SO₄/silica gel, 0.9 g of silica gel, 3 g of 2% KOH/silica gel and 0.9 g of silica gel. The hexane solution added with a cleanup spike was applied to a multilayer silica gel column, and eluted with 300 ml of hexane. After concentration, the fluid concentration was added with the syringe spike and analyzed by GC-MS.

Concentration Level of PCBs in the Sediments — For all congeners of PCBs, peak assignments were conducted based on the data presented by Matsumura *et al.*²³⁾ The concentration of PCBs was determined by an isotope dilution GC-MS method. PCB concentrations in sediments are expressed as the total concentration of congeners.

PCB homologues analyzed were M1CBs (M1), D2CBs (D2), T3CBs (T3), T4CBs (T4), P5CBs (P5), H6CBs (H6), H7CBs (H7), O8CBs (O8),

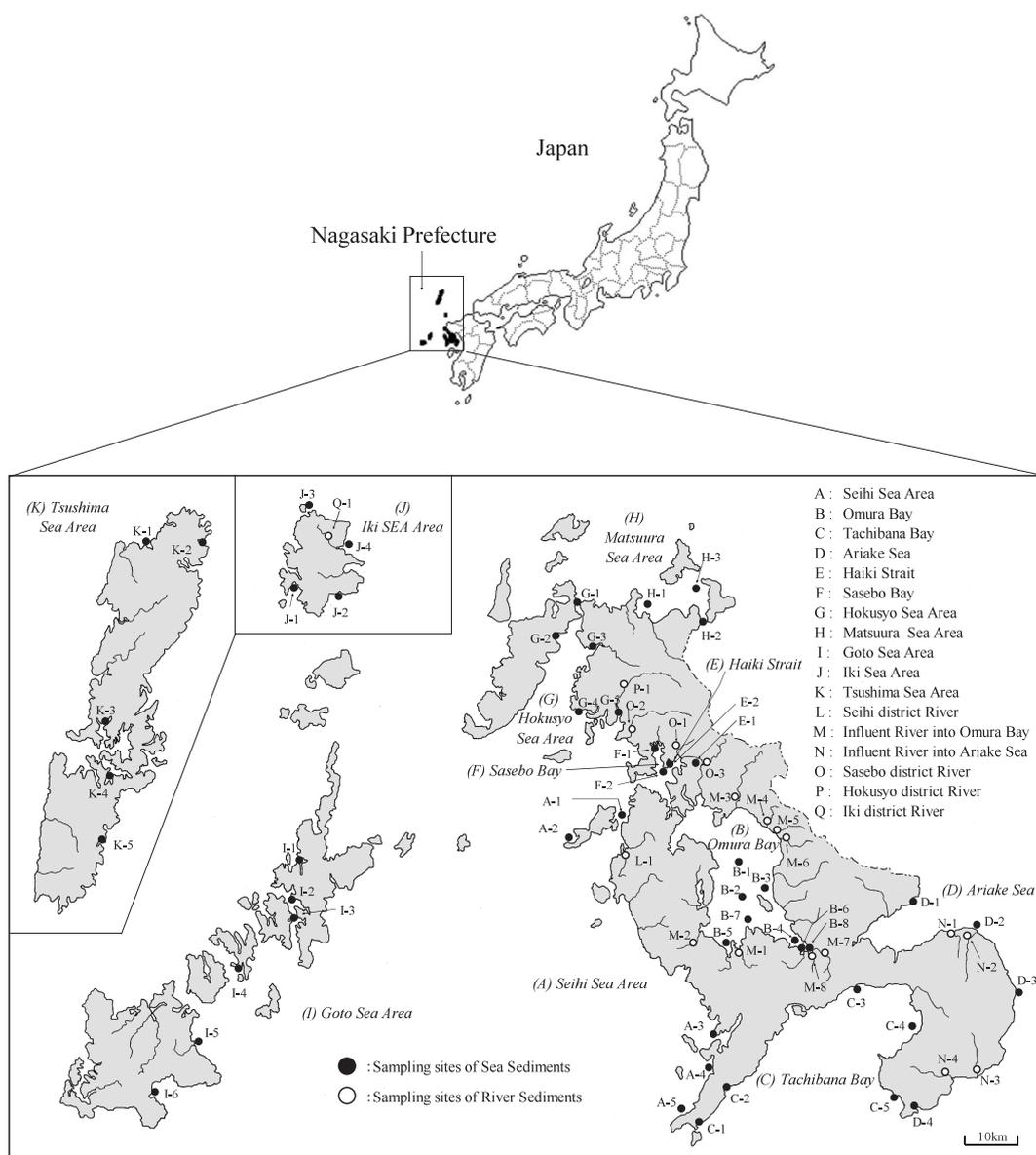


Fig. 1. Locations of Sampling Sites of Sediments in Nagasaki Prefecture

N9CBs (N9) and D10CB (D10). All PCBs congeners in sediment were determined according to peak ratio compared to cleanup spikes. For determination of the source contribution of PCBs, the data of 18 congeners such as IUPAC Nos. 18, 31, 28, 44, 70, 66, 101, 110, 118, 105, 153, 138, 174, 180, 170, 199, 203 and 194, which were major congeners in Kanechlor KC300–600,²⁰⁾ were used.

GC-MS System—The GC-MS system consisted of an HP-6890 GC system (Agilent, Santa Clara, CA, U.S.A.), a JMS-700 MS (JEOL Ltd., Tokyo, Japan) and an HT8-PCB capillary column (60 m × 0.25 mm, i.d., Kanto Chemical Co.). The oven temperature was initialized at 120°C, ramped at 20°C/min to 180°C, at 2°C/min to 260°C, then

at 5°C/min to 300°C (9 min).²³⁾ The temperature of the injector and the ion source were 280°C. The interface temperature was set at 300°C. Helium, flowing at 1.0 ml/min, was used as carrier gas. The electron impact ionization energy was 38 eV. A 1- μ l portion of the final solution was injected under split-less mode. Selected ion monitoring (SIM) mode was used and the resolution was kept higher than 10000 (10% valley). Procedural and instrument blanks were measured before sediment analysis. Retention times of congeners in sediments were compared with reference standards in order to identify them, according to the previous report.²³⁾ Moreover, the specific isotope ratios for each congener were checked (within

15%). The recovery of cleanup spikes (calculated using syringe spike) for each congener in sediment samples ranged from 75 to 106%, except IUPAC No. 3 (4-chloro-[¹³C]-labeled biphenyl) with 47% of recovery. The method detection limit (MDL) for individual congeners was 2 pg/g. The value of analytical blank for the individual congeners was less than MDL (2 pg/g).

A CMB Method—For determination of the source contribution of PCBs in sediments, the CMB method with the composition ratio of major congeners in Kanechlor KC300–600 was used. The basic principle of the CMB method is that measured profiles can be reproduced by the linear combinations of several sources. The profiles of 24 congeners, major components of Kanechlor KC300–600, were determined. Software, CMB8J Ver.0.96, was used for the CMB method.²²⁾

RESULTS AND DISCUSSION

Concentration Level of PCBs in the Sediments

The concentration levels of PCBs are shown in Table 1 and Fig. 2. PCBs were detected in all sediments studied and the concentrations varied considerably in the range of 0.00033–0.035 µg/g (river sediments, $n = 18$) and 0.0011–2.5 µg/g (sea

sediments, $n = 49$). The concentration levels of sea sediments were higher than those of river sediments ($p = 0.053$), with average concentrations of 0.12 µg/g for sea sediments and 0.0053 µg/g for river sediments. The sites showing the highest concentration of PCB levels in the sea and river sediments were I-5 (2.5 µg/g) and N-3 (0.035 µg/g), respectively.

As shown in Fig. 2, among the sea sediments (A–K), the PCB levels of the port areas such as A, G, I and J, were higher than those of bay areas such as B, C and D except F. It was expected that the PCB levels of bay areas would be higher than those of port areas, because PCBs in port areas would be diffused over a larger area than those in bay areas by influence of ocean currents. However, the opposite situation was observed in the area F. This might be due to the continuous input of PCBs from the paint of ships in shipyards located neighbored on the port area F. Sediment properties may be thought to be one of the most influential factors of PCB concentration. The ignition loss of sediments and water depth at sampling sites are summarized in Table 1. No relation between the ignition loss and PCB concentrations in the sediments could be found, although the PCB concentrations of the sediments with high clay content were higher than those with high sand content (data not shown). Pan

Table 1. PCB Concentrations in Sediments and Sample Properties

Water area	Concentration, µg/g		Ignition loss % of dry weight		Water depth, m	
	Mean	(range)	Mean	(range)	Mean	(range)
Total sea areas ($n = 49$)	0.12	(0.0011 – 2.5)	8.8	(2.5 – 29.6)	10.3	(3.0 – 24.0)
Total river areas ($n = 18$)	0.0053	(0.00033 – 0.035)	6.5	(1.9 – 18.1)	—	—
A ($n = 5$)	0.20	(0.0024 – 0.94)	6.7	(4.2 – 10.6)	8.3	(5.3 – 11.0)
B ($n = 8$)	0.0049	(0.0040 – 0.0082)	13.8	(8.2 – 29.6)	14.5	(5.0 – 21.0)
C ($n = 5$)	0.0035	(0.0011 – 0.0084)	5.1	(2.5 – 6.7)	7.7	(3.9 – 19.2)
D ($n = 4$)	0.0078	(0.0015 – 0.021)	6.1	(4.1 – 10.8)	6.7	(3.2 – 8.6)
E ($n = 2$)	0.033	(0.0059 – 0.061)	6.0	(3.0 – 9.0)	7.9	(3.7 – 12.0)
F ($n = 2$)	0.14	(0.081 – 0.19)	8.7	(7.6 – 9.7)	16.5	(11.6 – 21.3)
G ($n = 5$)	0.10	(0.0061 – 0.44)	12.8	(6.2 – 19.3)	6.3	(3.0 – 9.0)
H ($n = 3$)	0.0037	(0.0021 – 0.0058)	10.8	(9.0 – 13.6)	20.7	(18.0 – 24.0)
I ($n = 6$)	0.43	(0.0017 – 2.5)	6.5	(4.7 – 10.0)	14.7	(5.0 – 23.0)
J ($n = 4$)	0.27	(0.0037 – 0.89)	8.1	(5.4 – 10.5)	7.6	(7.0 – 9.0)
K ($n = 5$)	0.028	(0.0011 – 0.064)	7.7	(6.0 – 9.8)	5.5	(3.7 – 8.5)
L ($n = 1$)	0.00093		5.5		—	—
M ($n = 8$)	0.0038	(0.00033 – 0.019)	7.2	(2.3 – 18.1)	—	—
N ($n = 4$)	0.011	(0.0017 – 0.035)	7.6	(4.5 – 11.7)	—	—
O ($n = 3$)	0.0054	(0.0029 – 0.0082)	3.9	(1.9 – 6.8)	—	—
P ($n = 1$)	0.0021		6.0		—	—
Q ($n = 1$)	0.002		7.0		—	—

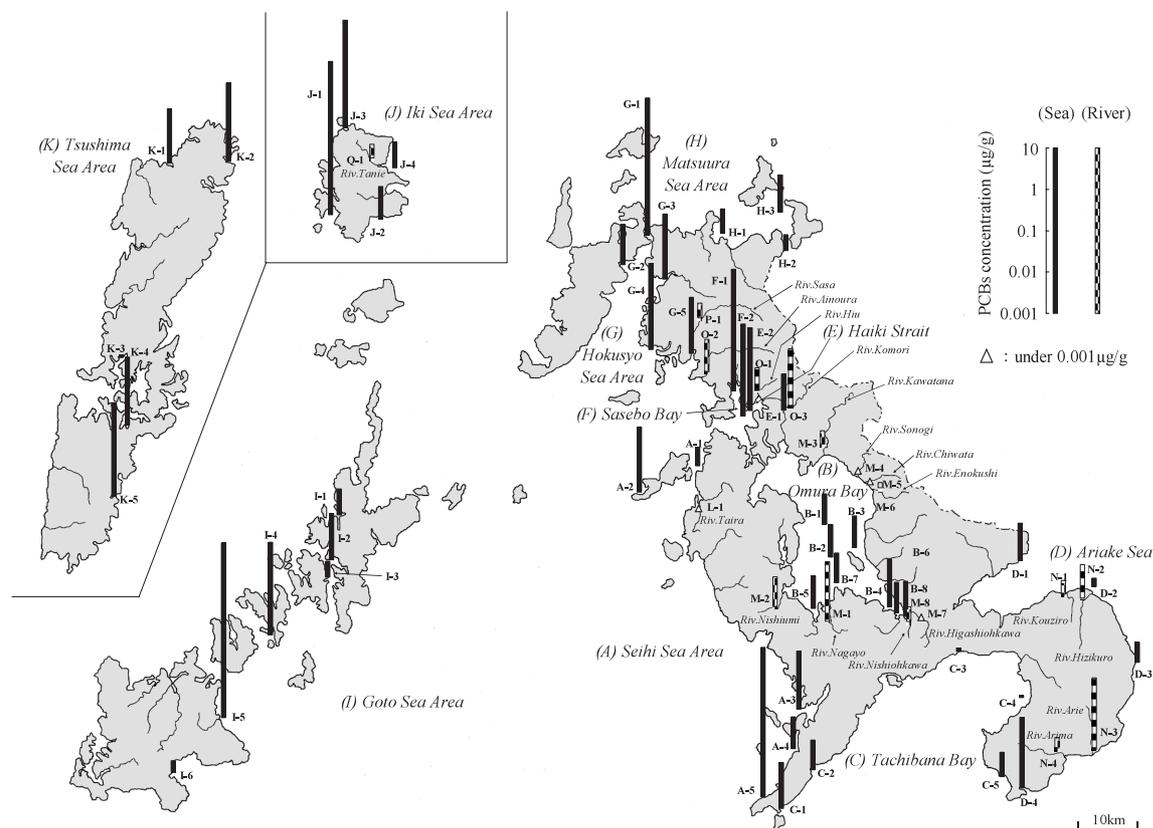


Fig. 2. PCBs Concentrations in Sediments at Each Sampling Site on Map

et al. reported that Σ PCDD/Fs contents were generally in the following sediment type order: organic matter enriched clay > sand-silt-clay and silty clay > clayey silt and silty sand.²⁴⁾ The same trend for PCB was observed in our study.

Japan's Governmental Ministry of the Environment routinely has been sampling at 60 locations distributed all over Japan and analyzes PCBs in the sediments.^{11–14)} In 2004, the determination of PCB levels in the sediments at 62 sea areas was performed.¹⁴⁾ The PCB levels ranged from 3.9×10^{-5} to $5.6 \mu\text{g/g}$ (medium: $0.0095 \mu\text{g/g}$). In the last four years, PCB levels in Japan have been almost constant and the results obtained in our study are comparable with them. As a unique case, the PCB concentrations in D and its influent river area (N) were $0.0078 \pm 0.0045 \mu\text{g/g}$ and $0.011 \pm 0.0080 \mu\text{g/g}$, respectively. In a previous report, the PCB concentrations in sea sediments at similar sites (the tidal flat sediments in Ariake Sea) in 1999–2000 were $0.030 \mu\text{g/g}$.¹⁹⁾ River sediments (sub-microgram level) contained higher PCB concentrations than sea sediments and our results in this area showed the same trend. Moreover, the local study on PCB levels in a limited part of

Nagasaki Bay (site A-3), was performed in 1983 by Maruyama *et al.*,²⁵⁾ where an adjacent shipyard was one of the PCB sources. The PCB level was $0.10 \mu\text{g/g}$ (median), ranging from 0.005 to $11.0 \mu\text{g/g}$ ($n = 52$) and a few samples located near the shipyard drain showed especially high level of PCBs (more than $10 \mu\text{g/g}$). Since the PCB level of A-3 was $0.015 \mu\text{g/g}$, it can be presumed that unchanged PCB contamination has been present for 24 years.

Pollution Characteristics Profiles of the PCB Homologues

The major homologues for KC300, 400 and 500 were T3, T4 and P5, respectively, and those for KC600 were H6 and H7. The profiles of PCB homologues in the sediments were compared with those of KC300–600 and the profiles of PCB homologues for KC300–600 and sediments in sea and river areas are shown in Fig. 3. On the whole, the profiles of PCB homologues for total sea sediments seemed to be highly similar to KC600 and that for total river sediments, relatively similar to KC500. Among all sampling sites, the profiles of PCB homologues at A, F, I, and J were highly similar to KC600, and the profiles at sites of N, and P

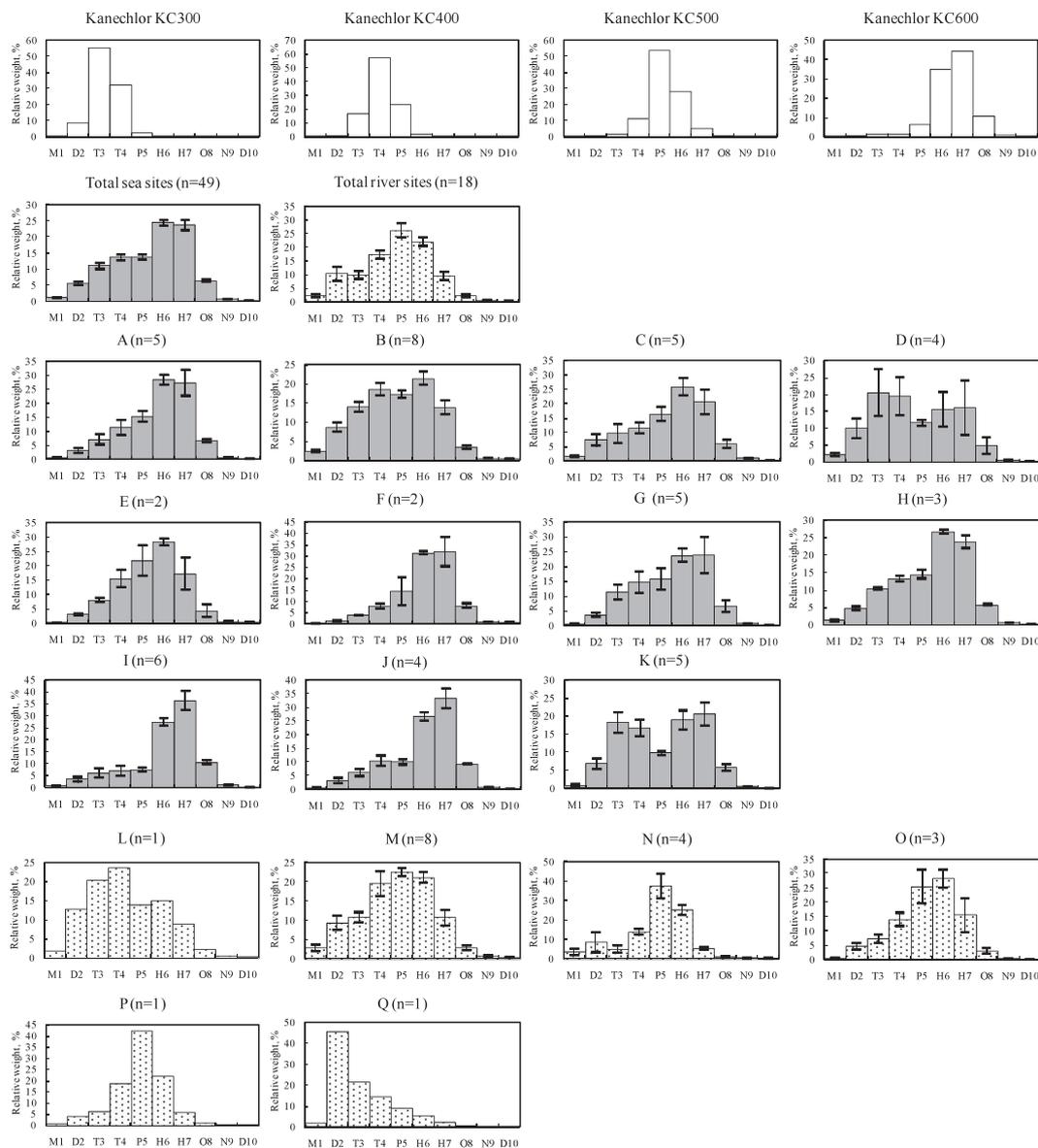


Fig. 3. Profiles of PCB Homologues in Kanechlor KC300–600 and Sediments for Total Sea and River Sites, and Each Water Area (A-Q)

were highly similar to KC500. However, in other water areas multiple-pollution by Kanechlors was suspected since the profile of PCB homologues did not fit with that of a single Kanechlor product. This result suggested that KC600 might be one of the major sources of PCBs in port areas, since KC600 has been used in the past in paint for the bottom of ships. In a previous report, the profile of PCB homologues in Nagasaki Bay (A-3), one of sampling sites of area A, also resembled KC600.²⁵⁾

The Ministry of the Environment in Japan reported that the profiles of PCB homologues at the sites highly polluted with PCBs in Japan were similar to that of KC400.^{11–14)} This difference might be due to the different source of PCBs in Nagasaki

Prefecture.

Several river sediments showed relatively high concentration of PCBs and the profiles of PCB homologues were similar to KC500. On the other hand, a specific profile of PCB homologues with a high content of D2 was observed at site Q. The major congener of D2 at the site Q was 3,3'-dichlorobiphenyl (#11). Litten *et al.* reported that the non-Arochlor PCB congener, #11 was ubiquitously found in the harbor as well as our result. Moreover, this compound was to be associated with pigment manufacture and unlikely to be a dechlorination product.²⁶⁾ There is not the pigment manufacture near site Q. So the long-range atmospheric transport of PCBs might be suspected, although the

reason for this phenomenon was not clear. Additionally, the similarity of the PCB profile with Kanechlor could not be observed in a few sediments of river areas, due to their low concentration of PCBs.

Determination of the Source Contribution by a CMB Method

A profiling method of PCB homologues is useful to predict the pollution source of PCBs, when the sediment was dominated by a single Kanechlor ingredient such as KC300, KC400, KC500 or KC600. However, the contribution of multiple-Kanechlor or combusive PCBs makes it difficult to identify the pollution source by the profiling method. In this case the source contribution by a CMB method using the composition percentages of major congeners of Kanechlor was performed.¹⁶⁾ The composition percentages of 18 major congeners in KC300–600 standard solutions were determined (Table 2) and used for calculation of the source contribution.

The source contributions of total sea and river sediments and each water area (A-Q) are shown in Fig. 4. The source contribution of the sites showed a complicated profile of PCB homologues that could also be measured. The parameters, χ^2 value, r^2 and %mass were in the range 2.9–23.8, 0.937–0.983 and 90.0–101.9%, respectively. As a result, it turned out that the major pollutant sources in the total sea and river areas were KC600 (ca 60% of contribution)

and KC500 (ca 50% of contribution), respectively. Whereas the high contribution of KC600 was found in most sea areas, the contribution of KC600 was less than 50% at sites B, D and E. In Ariake Sea (corresponding area D), a large contribution from KC400 was observed in sea and river sediment. In a previous report, KC300 and 400 were presumed to be the source of contamination of PCBs by a fingerprint method.¹⁹⁾ In the fingerprint method, correlation coefficient between the congeners content in sample and Kanechlors was calculated. This finding agreed well with the results in our study. On the other hand, the contribution of KC600 in river areas was lower than that in sea water areas and around 50% or more contribution of KC500 was observed in river areas M, N, O and P. Area Q showed a specific result that the contribution of KC300 was more than 60%. The reason for this phenomenon could not be explained; specific source contribution may be considered. As source contribution in river sediments was more complicated than that in sea sediments, multiple-pollution should be considered in river water areas.

In conclusion, the concentration levels of PCBs in sea and river sediments sampled from 2000 to 2005 in Nagasaki Prefecture were determined. The pollution characteristics were studied by the profiles of PCB homologues and the CMB method using the composition percentages of major congeners of Kanechlor. The profiles of PCB homologues in sea

Table 2. Composition Percentages of Major Congeners in Kanechlor KC300–600

Congeners	IUPAC No.	Composition %			
		KC-300	KC-400	KC-500	KC-600
2,2',5-Trichlorobiphenyl	#18	19.50	6.42	0.55	0.42
2,4',5-Trichlorobiphenyl	#31	14.12	6.84	0.43	0.27
2,4,4'-Trichlorobiphenyl	#28	16.14	6.07	0.41	0.23
2,2',3,5'-Tetrachlorobiphenyl	#44	6.66	11.17	2.42	0.20
2,3',4',5'-Tetrachlorobiphenyl	#70	6.72	16.06	4.52	0.32
2,3',4,4'-Tetrachlorobiphenyl	#66	5.45	11.87	0.98	0.17
2,2',4,5,5'-Pentachlorobiphenyl	#101	0.62	4.96	13.09	3.16
2,3,3',4',6-Pentachlorobiphenyl	#110	0.60	5.72	13.74	1.35
2,3',4,4',5-Pentachlorobiphenyl	#118	0.38	4.40	9.16	0.62
2,3,3',4,4'-Pentachlorobiphenyl	#105	0.23	2.51	3.60	0.20
2,2',4,4',5,5'-Hexachlorobiphenyl	#153	0.08	0.40	7.85	12.41
2,2',3,4,4',5'-Hexachlorobiphenyl	#138	0.07	0.65	10.47	6.77
2,2',3,3',4,5,6'-Heptachlorobiphenyl	#174	0.02	0.01	0.92	9.03
2,2',3,4,4',5,5'-Heptachlorobiphenyl	#180	0.03	0.03	2.29	20.87
2,2',3,3',4,4',5-Heptachlorobiphenyl	#170	0.01	0.03	1.31	5.42
2,2',3,3',4,4',5,5'-Octachlorobiphenyl	#199	0	0	0.23	3.78
2,2',3,4,4',5,5',6-Octachlorobiphenyl	#203	0	0	0.19	2.65
2,2',3,3',4,4',5,5'-Octachlorobiphenyl	#194	0	0	0.45	3.89

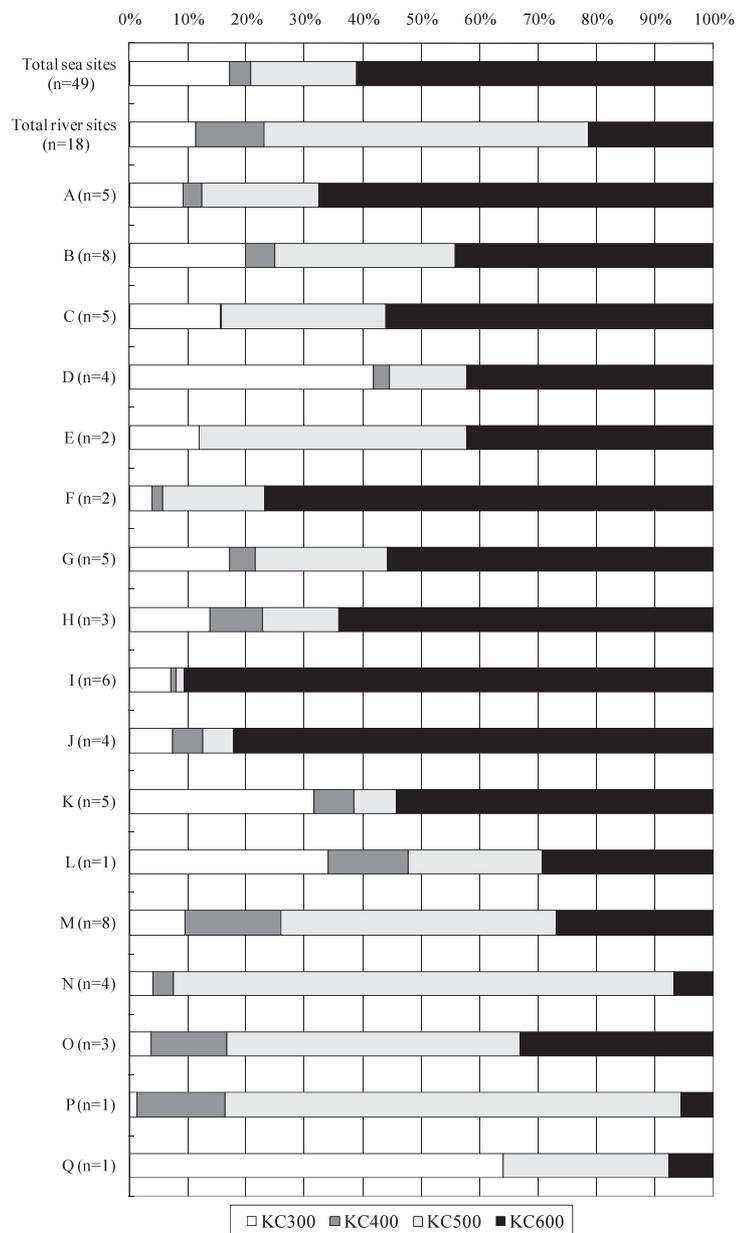


Fig. 4. Source Contributions of Kanechlors in Sediments for Total Sea and River Sites, and Each Water Area (A-Q) by the CMB Method

and river sediments were similar to those of KC600 and KC500, respectively. Moreover, the results obtained by the CMB method agreed well with those results. Therefore, in Nagasaki Prefecture, it is presumed that there is major input from KC600 and KC500. From now on, it may be important to monitor the PCB concentrations continuously and to clarify the effects on human health.

Acknowledgement The authors acknowledge to Dr. Gwyn Lord, School of Biological and Chemical Sciences, University of London, for his kind review of this article.

REFERENCES

- 1) Noma, Y., Ishikawa, I., Nose, K., Minetomamatsu, K., Takigami, H., Sakai, S., Izumisawa, S. and Kaburaki, Y. (2004) Chemical characterization of PCBs and dioxins in the waste PCB Stockpiles. *J. Environ. Chem.*, **14**, 501–518.
- 2) Imamoglu, I. and Christensen, E. R. (2002) PCB sources, transformations, and contributions in recent Fox River, Wisconsin sediments determined from receptor modeling. *Water Res.*, **36**, 3449–3462.
- 3) Sivery, J. D. and Lee, C. M. (2007) Polychlorinated biphenyl contamination trends in Lake Hartwell, South Carolina (USA): Sediment recovery profiles

- spanning two decades. *Chemosphere*, **66**, 1821–1828.
- 4) Katsoyiannis, A. (2006) Occurrence of polychlorinated biphenyls (PCBs) in the Soulou stream in the power generation area of Eordea, northwestern Greece. *Chemosphere*, **65**, 1551–1561.
 - 5) Maskaoui, K., Zhou, J. L., Zheng, T. L., Hong, H. and Yu, Z. (2005) Organochlorine micropollutants in the Jiulong River Estuary and Western Xiamen Sea, China. *Mar. Pollut. Bull.*, **51**, 950–959.
 - 6) Nagayama, J., Kuratsune, M. and Masuda, Y. (1976) Determination of chlorinated dibenzofurans in Kanechlors and “Yusho oil”. *Bull. Environ. Contam. Toxicol.*, **15**, 9–13.
 - 7) Miyata, H., Kashimoto, T. and Kunita, N. (1977) Detection and determination of polychlorodibenzofurans in normal human tissues and Kanemi rice oils caused “Kanemi Yusho”. *J. Food Hyg. Soc. Jpn.*, **18**, 260–265.
 - 8) Morita, M., Nagayama, J. and Akiyama, K. (1977) Detailed examination of polychlorinated dibenzofurans in PCB preparations and Kanemi Yusho oil. *Bull. Environ. Contam. Toxicol.*, **18**, 67–73.
 - 9) Buser, H. R., Rappe, C. and Gara, A. (1978) Polychlorinated dibenzofurans (PCDFs) found in Yusho oil and used in Japanese PCB. *Chemosphere*, **7**, 439–449.
 - 10) Yao, Y., Takasuga, T., Masunaga, S. and Nakanishi, J. (2002) Detailed on the levels polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans and polychlorinated biphenyls in Yusho rice oil. *Chemosphere*, **46**, 1461–1469.
 - 11) Ministry of the environment, Government of Japan (2001) Chemicals in the environmental, Report on environmental survey and wildlife monitoring of chemicals, Fiscal Year 2001, http://www.env.go.jp/chemi/kurohon/http2001/sec1_6h2.html
 - 12) Ministry of the environment, Government of Japan (2002) Chemicals in the environmental, Report on environmental Survey and Monitoring of chemicals, Fiscal Year 2002, http://www.env.go.jp/chemi/kurohon/http2002/sec1_6h2.html
 - 13) Ministry of the environment, Government of Japan (2003) Chemicals in the environmental, Report on environmental Survey and Monitoring of chemicals, Fiscal Year 2003, <http://www.env.go.jp/chemi/kurohon/http2003/xls/3-2-100.xls>
 - 14) Ministry of the environment, Government of Japan (2004) Chemicals in the environmental, Report on environmental Survey and Monitoring of chemicals, Fiscal Year 2004, <http://www.env.go.jp/chemi/kurohon/http2004/xls/3-2-100.xls>
 - 15) Tashiro, Y., Takahira, K., Osada, H., Fujii, H. and Tokuyama, A. (2004) Distribution of polychlorinated bisphenyls (PCBs), lead, and cadmium in Manko Tidal Flat, Okinawa. *Limnology*, **5**, 177–183.
 - 16) Okumura, Y., Yamashita, Y., Kohno, Y. and Nagasaka, H. (2004) Historical trends of PCDD/Fs and CO-PCBs in a sediment core collected in Sendai Bay, Japan. *Water Res.*, **38**, 3511–3522.
 - 17) Naito, W., Jin, J., Kang, Y. S., Yamamuro, M., Masunaga, S. and Nakanishi, J. (2003) Dynamics of PCDDs/DFs and coplanar-PCBs in an aquatic food chain of Tokyo Bay. *Chemosphere*, **53**, 347–362.
 - 18) Ikenaka, Y., Eun, H., Watanabe, E., Kumon, F. and Miyabara, Y. (2005) Estimation of sources and inflow of dioxins and polycyclic aromatic hydrocarbons from the sediment core of Lake Suwa, Japan. *Environ. Pollut.*, **138**, 529–537.
 - 19) Nakata, H., Miyawaki, T. and Sakai, Y. (2002) Concentrations and isomer compositions of polychlorinated biphenyls (PCBs) in tidal flat sediments from the Ariake Sea and their implications for sources and distribution. *J. Environ. Chem.*, **12**, 127–134.
 - 20) Takasuga, T., Inoue, T. and Ohi, E. (1995) All congener specific analytical method for polychlorinated biphenyls (PCBs) with various chromatographic clean-up and HRGC/HRMS. *J. Environ. Chem.*, **5**, 647–675.
 - 21) Kim, K. S., Hirai, Y., Kato, M., Urano, K. and Masunaga, S. (2004) Detailed PCB congener patterns in incinerator flue gas and commercial PCB formulations (Kanechlor). *Chemosphere*, **55**, 539–553.
 - 22) Hayakari, S. and Hanaishi, R. (2001) Introduction of spreadsheet application macros for environmental data analytical examples (II)—macro for CMB analysis—. *J. Jpn. Soc. Atmos. Environ.*, **36**, 39–45, <http://www.jomon.ne.jp/hayakari/>
 - 23) Matsumura, C., Tsurukawa, M., Nakano, T., Ezaki, T. and Ohashi, M. (2002) Elution order of all 209 PCBs congeners on capillary column “HT8-PCB”. *J. Environ. Chem.*, **12**, 855–865.
 - 24) Pan, J., Yang, Y. L., Chen, D. Z., Xu, Q., Tang, H., Li, Y., Nie, L. M., Jiang, K. and Xi, D. L. (2008) Distribution characteristics and source analysis of dioxins in sediments and mussels from Qingdao coastal sea. *Chemosphere*, **70**, 1699–1706.
 - 25) Maruyama, K., Sahrul, M., Tanabe, S. and Tatsukawa, R. (1983) Polychlorinated biphenyl pollution from shipbuilding in Nagasaki Bay, Japan. *Ecotoxicol. Environ. Saf.*, **7**, 514–520.
 - 26) Litten, S., Fowler, B. and Luszniak, D. (2002) Identification of a novel PCB source through analysis of 209 congeners by US EPA modified method 1668. *Chemosphere*, **46**, 1467–1459.