Bull. Environ. Contam. Toxicol. (1989) 42:589–594

Bulletin of Environmental Contamination and Toxicology

Levels of Chlordane in Water and Sediment of Rivers around Saga City, Japan

Yukio Hirai and Katsumaro Tomokuni

Department of Community Health Science, Saga Medical School, Nabeshima, Saga 840-01, Japan

Both cis-α-chlordane and trans-γ-chlordane (1,2,4,5,6,7,8,8-octachloro-3a,4,7,7a-tetrahydro- 4,7-methanoindane,$C_{10}H_6Cl_8$) are main components of the technical chlordane(Sovocool et al. 1977) which had been mainly used as a pesticide for controling the termite until September 1986 in Japan. The characteristic features of chlordane are that it is much more stable in the environment such as sediment(Oloffs et al. 1978) and that its bioaccumulation in some species of bacteria, freshwater invertebrates, and marine fish is large (WHO 1984).

In the present study, we investigated the residues of chlordane in our living environments which are Saga city and its surroundings. Saga city is located in the middle of a paddy field sandwitched between a mountain district in the north and Ariake sea in the south. In this paper, we report the levels of chlordane in water and sediment of the rivers which originate in the mountain district, flow down to the south through Saga city, and pour into Ariake sea.

MATERIALS AND METHODS

Surface water was collected in 1 L glass bottle. River sediment was collected in 50 mL glass bottle. The pretreatment of the water sample(0.5-1.0 L) for the determination of chlordane using GC/MS was done according to the method of Miyazaki et al.(Miyazaki et al. 1985). This method consists of extraction with n-hexane, partitioning with acetonitrile, extraction with n-hexane, silicagel column chromatography and concentration by evaporation. The pretreatment of the sediment sample(1-10 g) consisted of extraction with acetonitrile, extraction with n-hexane, silicagel-column chromatography and concentration by evaporation.

Send reprint to Dr Y. Hirai at the above address.

The procedure for the micro cleanup and concentration developed by us (Hirai and Tomokuni 1987) was applied at the final step to concentrate the samples into 20-30 μL in the capillary.

GC/MS was used to determine the total amount of trans- and cis-chlordane. The apparatus used was a JEOL-DX300 double focusing GC/MS system coupled with a JEOL-DA5000 computer system(JEOL LTD., Tokyo, Japan). The MS system was operated in the mode of electron impact ionization and selected ion monitoring (SIM) of positive ions. As a stable isotope labeled analog of chlordane was not available, the determination was done by absolute calibration method. The molecular ion (M, m/z=410), and the fragment ion (M-Cl, m/z=375) and its isomer ion (m/z=373) were employed for SIM. The determination was carried out mainly by using the mass fragmentograms obtained by monitoring m/z=373 or 375. Other analytical conditions were described elsewhere (Hirai and Tomokuni 1987).

The relative standard deviation of the determination by GC/MS was less than 10% when 2.8 ng of trans-chlordane was injected 7 times. The recovery of chlordane at the pretreatment of the sample was about 50%. The detected values were multiplied by two to obtain analytical values. The analytical values were expressed in one significant figure. The limit of determination was 0.2 ng/L for river water and 0.02 ng/g(dry weight) for river sediment.

RESULTS AND DISCUSSION

We investigated first the levels of chlordane in the water of both water supplying rivers and drainage rivers. Sampling points are shown in Fig. 1 with open circles and numbers. The first sample was collected at Hokusan dam(A). The dam stores 2×10^7 m^3 of fresh water for irrigation, industry, producing electric power, and tap water of the residents of Saga city. The sampling points 2 to 4 are located on the upstream of Kase river(B) surrounded by the forest where the inflow of waste water is smaller.Tafuse river(C) separates from Kase river near sampling point 4. The sampling points 5 and 6 are located on the upper side than the water treatment plant(W) built at the side of Tafuse river. The river water is treated there for domestic use. The treated water is supplied for about 170,000 residents of Saga city. Tafuse river flows through the urban area branching into small streams. There are many small streams which are not described in Fig. 1. The small streams flow absorbing waste water from houses and industries. Honjo-e river(D), Hatta-e river(E) and Saga-e river(F) are the main drainage

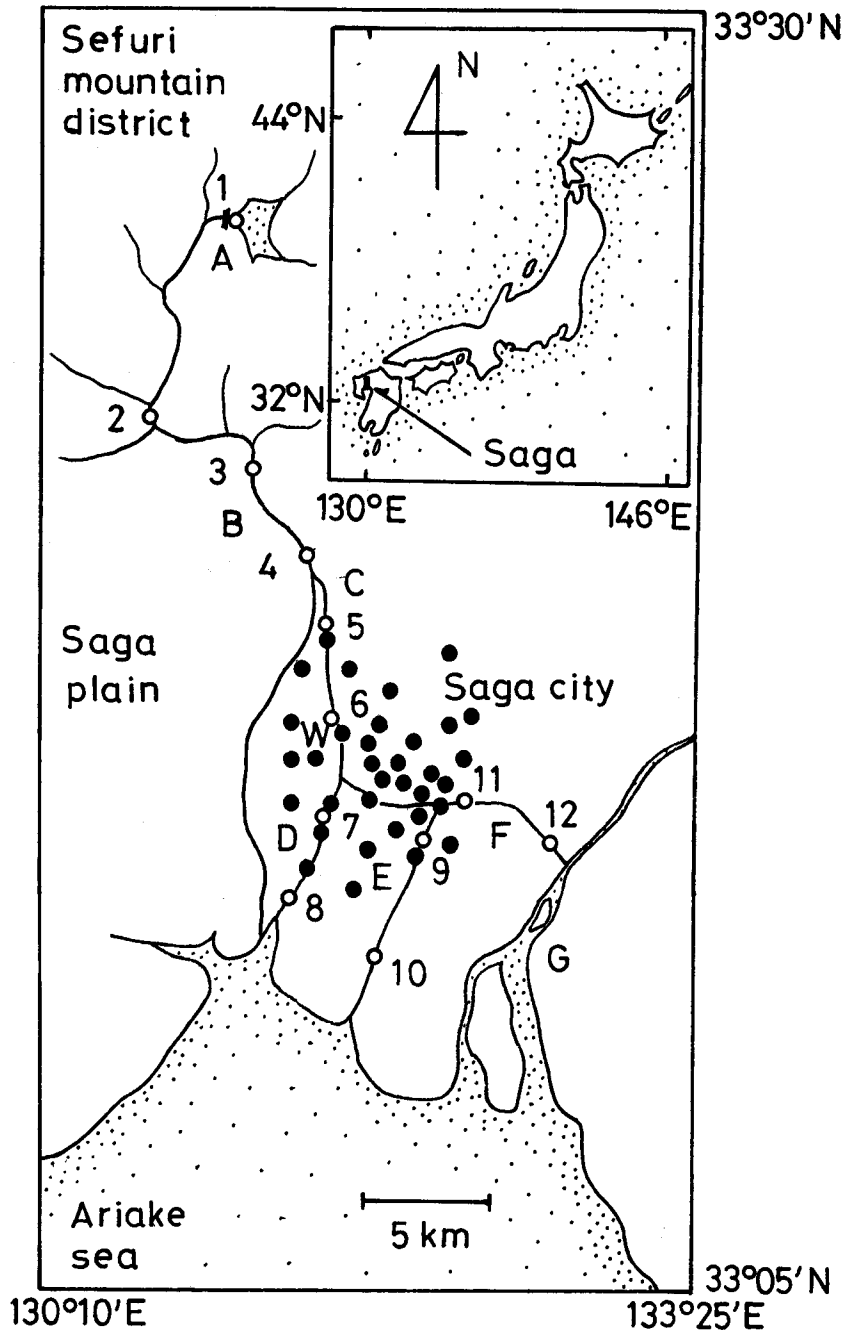

Figure 1 Sampling points of river water (O), and river water and river sediment (●) around Saga city
A; Hokusan dam, B; Kase river, C; Tafuse river, D; Honjo-e river, E; Hatta-e river, F; Saga-e river, G; Chikugo river, W; water treatment plant

river of the polluted streams. The sampling points 7 and 8, 9 and 10, and 11 and 12 are located on these three drainage rivers respectively.Both Honjo-e river and Hatta-e river pour directly into Ariake sea. Saga-e river pours into Chikugo river(G).

Table 1 shows the results. The investigation was done twice,i.e.,December in 1987 and March in 1988. Chlordane was not detected in the water of water supplying rivers at the mountain district(sampling points 1 to 4). The levels of chlordane were low even at an urban area where the inflow of waste water from houses and industries was smaller(sampling points 5 to 6). On the other hand, chlordane was slightly detected in all water samples collected at the drainage rivers(sampling points 7 to 12). The increase in concentration of chlordane was estimated to be due to the contamination of the streams in the urban area of Saga city.

Table 1 Concentration of chlordane in water supplying river and drainage river around Saga city

Sampling point	Concentration of chlordane in ng/L	
Water supplying river	December 1987	March 1988
(1)	--	n.d.
(2)	n.d.	n.d.
(3)	n.d.	n.d.
(4)	n.d.	n.d.
(5)	n.d.	n.d.
(6)	n.d.	n.d.
Drainage river		
(7)	9	7
(8)	1	4
(9)	4	7
(10)	1	3
(11)	--	6
(12)	--	4

n.d.; less than the limit of determination (0.2 ng/L)
-- ; not determined

We investigated second the levels of chlordane in water and sediment of the rivers as well as small streams in Saga city. Thirty four of both river water and sediment samples were collected on January 26 to 29 in 1988. The sampling points are shown in Fig. 1 with closed circles.

Figure 2 shows the results. The concentration of chlordane in water ranged from n.d. to 20 ng/L(Fig.2A). The median was 3 ng/L, and its level was similar to the

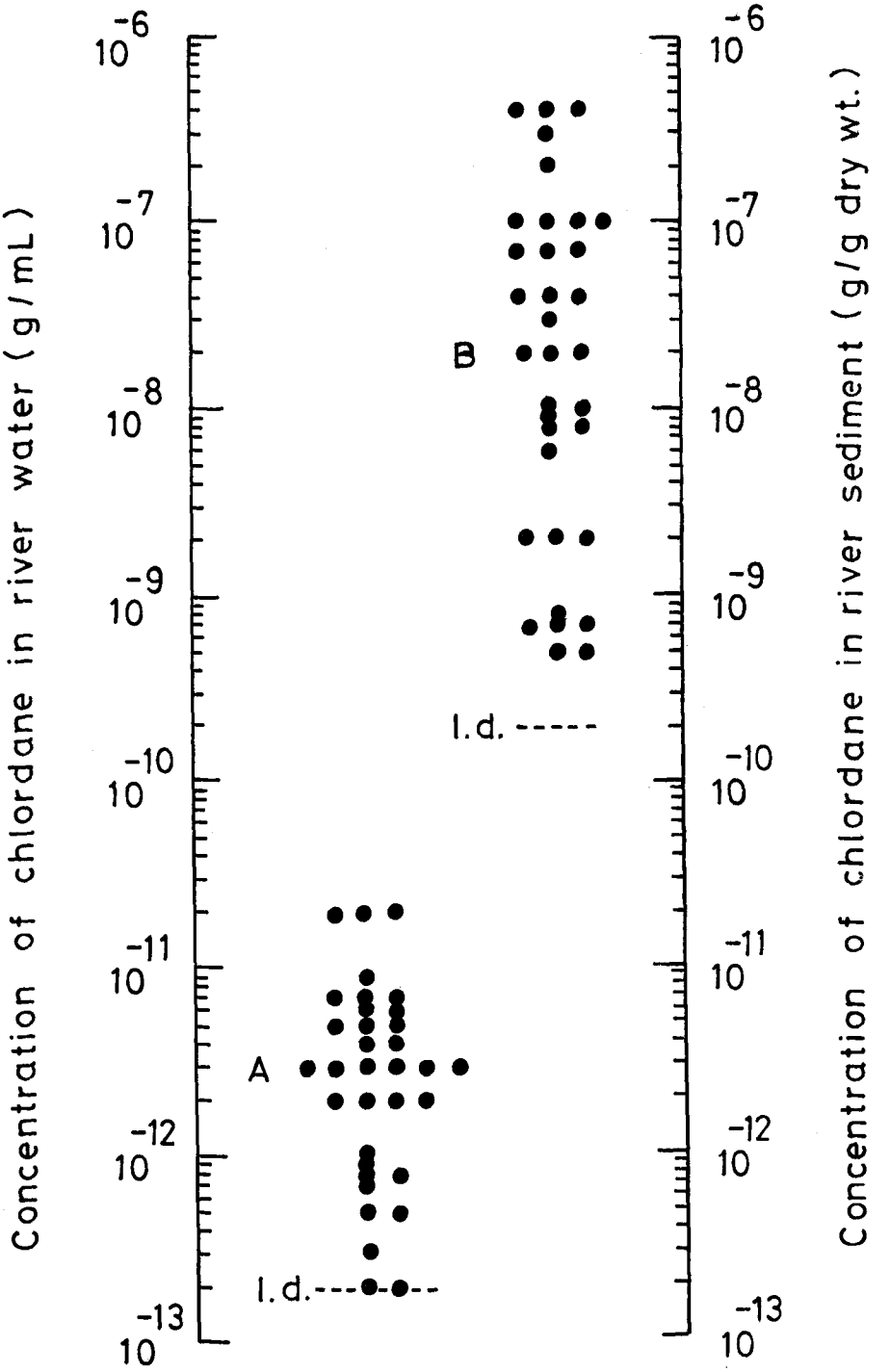

Figure 2 The levels of chlordane in river water (A) and river sediment (B) around Saga city
l.d.; limit of determination

level of trans-γ-chlordane obtained by monitoring the lower Mississippi river in 1974(Brodtmann 1976). The levels of chlordane in river sediment ranged from 0.5 to 400 ng/g(Fig. 2B). The median was 20 ng/g. The log of the concentration of chlordane in river water was correlated with the log of that in river sediment. The correlation coefficient was 0.53 when the concentration of chlordane of the samples showing n.d. was estimated to be 0.2 ng/L (detection limit). Particularly, the levels of chlordane were higher at the points where the pollution of the stream with waste water was apparent.

Further investigation is in progress to elucidate the origin of the chlordane in river water by monitoring the chlordane and other components of technical chlordane as well as their metabolites.

Acknowledgments. This work was supported in part by a Grant-in-Aid for Scientific Research (No.62770351) from the Ministry of Education, Science and Culture, Japan.

REFERENCES

Brodtmann NV Jr (1976) Continuous analysis of chlorinated hydrocarbon pesticides in the lower Mississippi river. Bull Environ Contam Toxicol, 15: 33-39.

Hirai Y, Tomokuni K (1987) Simple sample-pretreatment for GC/MS determination of residual chlordanes in river sediments. Bunseki Kagaku, 36: 817-819.

Miyazaki T, Yamagishi T, Matsumoto M (1985) Selected ion monitoring method for the determination of residues of chlordanes. J Food Hyg Soc Japan, 26: 371-379.

Oloffs PC, Albright LJ, Szeto SY (1978) Persistence of residues in water and sediment of a fresh-water lake after surface application of technical chlordane. J Environ Sci Health, B13(1): 47-58.

Sovocool GW, Lewis RG, Harless RL, Wilson NK, Zehr RD (1977) Analysis of technical chlordane by gas chromatography/mass spectrometry. Anal Chem, 49: 734-740.

WHO (1984) Environmental health criteria 34 "Chlordane".

Received May 9, 1988; accepted August 24, 1988.