

POPs Monitoring in Japan - Fate and Behavior of POPs -

Takeshi NAKANO¹, Minoru FUKUSHIMA², Yasuyuki SHIBATA³, Noriyuki SUZUKI³,
Yoshikatsu TAKAZAWA³, Yoshitoku YOSHIDA⁴, Noriya NAKAJIMA⁴,
Yasunori ENOMOTO⁴, Shinsuke TANABE⁵, Masatoshi MORITA³

¹Hyogo Pref. Inst. of Public Health & Env. Sci., Kobe

²Osaka City Inst. of Public Health & Env. Sci., Osaka

³National Inst. for Env. studies, Tsukuba

⁴Ministry of the Environment, Tokyo

⁵Ehime University, Matsuyama

Introduction

POPs monitoring by Japanese Ministry of the Environment (former Environment Agency) had continued from 1978 in the biological samples and from 1986 in the water and sediment samples until 2001. To cope with the Stockholm Convention, changing pollution levels, and the technological innovations, the activity was reframed into "POPs pollution investigation (POPs monitoring survey)" in 2002 taking into consideration the data accumulation and continuity.

Methods and Materials

In the POPs monitoring survey fiscal year 2002, 102 air samples from 34 points, 114 water samples from 38 points, 189 sediment samples from 63 points, 118 biological samples (fish, clams and birds in total) from 24 points were analyzed using HRGC/HRMS for PCBs, HCB, aldrin, endrin, DDTs, chlordanes, heptachlor, and HCHs.

Results and Discussion

Summary of Environmental levels

The best efforts to investigate POPs, compounds listed on the POPs convention and other related compounds, individually and with high sensitivity resulted in high frequency of POPs detection and determination in the samples. The case where the 25-percentile value was below the detection limit was only for the endrin in sediment. POPs level ranges in the air, water, sediment and biota are shown in Figure 1. The medium values in the air sample resided in the grades: for chlordane, HCB and PCBs, 100pg/m³; for DDTs, dieldrin and heptachlor 10pg/m³. In the water samples, PCBs and HCHs followed by chlordanes and DDTs are in relatively high levels. In the sediment, the level of PCBs was as high as in the order of 10000pg/g-dry followed by DDTs, chlordanes and HCB. In the biological samples, the levels of compounds are similarly ordered as in the sediment: the PCBs, DDTs and chlordane levels were high; levels of dieldrin and HCB were at least one order of the magnitude lower than these compounds. PCB congener and HCB level ranges in the air, water, sediment and biological samples are shown in Figure 3. The medium values for PCB resided in the grades of: for air, 100 pg/m³; water, 100pg/L; sediment, 10000pg/g-dry; biological samples, 10000pg/g-wet. For HCB, they were: for air, 100pg/m³; water, 10pg/L; sediment, 100pg/g-dry;

biological samples, 100pg/g-wet respectively. HCB levels compared with PCB were slightly lower in the air and water, and more than two orders of the magnitude lower in the sediment and biological samples. It is speculated that there is non-intentional emission load of PCB and HCB along with the environmental load originated from the past use of these industrial products. The Ministry of the Environment is now leading the investigation on the emission inventory of these compounds.

Accumulation from the water and sediment

Pollution interaction between the air and water environment is yet to be elucidated. On the other hand, water to sediment transition is accounted for by the physico-chemical properties of the elements. The increase in the accumulation seen is in the range of 10^3 for HCHs and 10^4 for

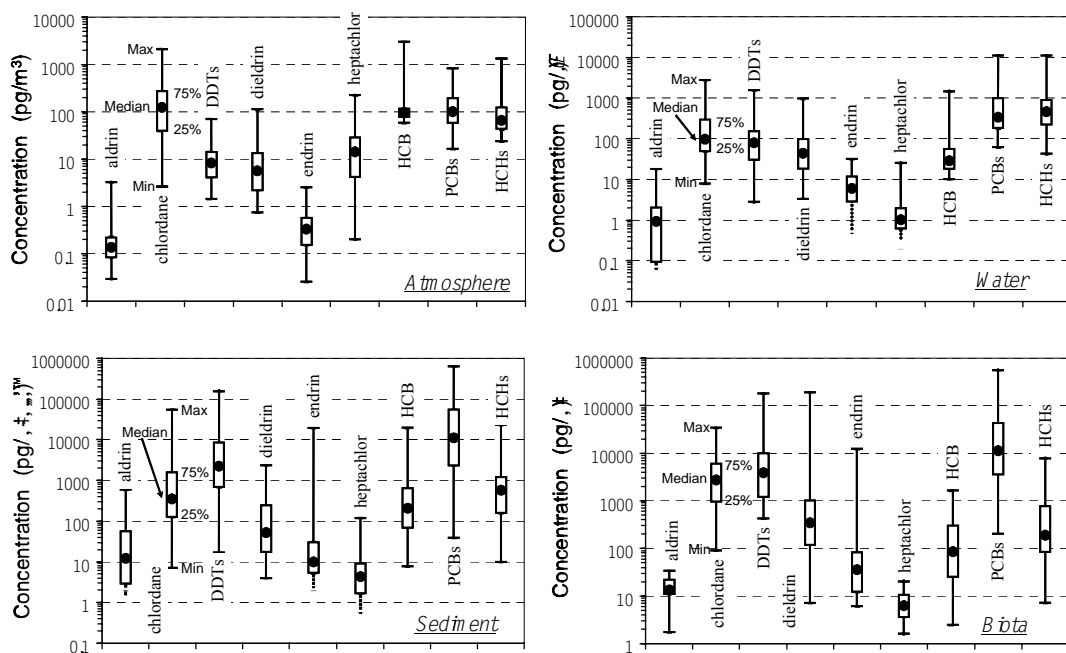


Figure 1: POPs level in Atmosphere, Water, Sediment and Biota. (Max, Min, Median, 25%, 75% value)

DDTs in average. However, the sediment/water concentration ratio for each compound varies greatly suggesting the effects of organic materials' contents. Water/organism concentration coefficients were similar to those of the water/sediment. In DDTs and HCB, however, difference between the species was observed and there was an upward trend along the trophic level.

Isomeric/congeneric composition change

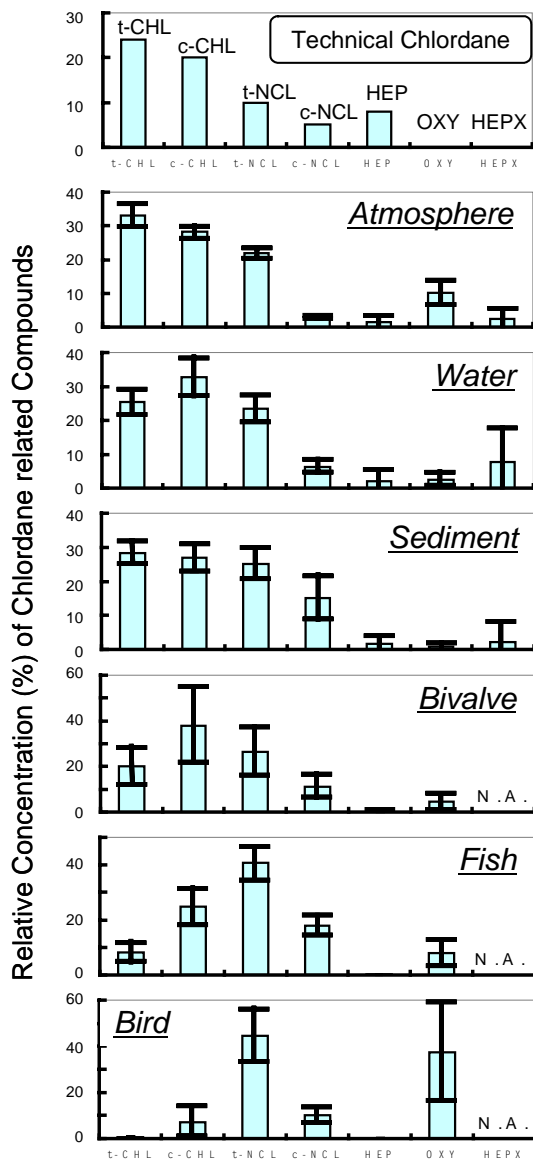


Figure 2: Congeneric profile of chlordane related compounds in Technical chlordane product, Atmosphere, Water, Sediment, Bivalve, Fish and Bird.

PCB Difference in vaporization pressure that affects the transfer into atmospheric phase or in precipitation characteristics among HCB and 209 congeners of PCBs is reflected in the isomeric/congeneric distribution patterns in the environment. Suzuki¹ indicated that the highly volatile HCB emitted to the air is mostly transferred out of the system by the atmospheric transportation only, while the compounds with lower vaporizing pressure tend to precipitate back on the land and sea. PCB congeneric patterns in air, water and sediment are almost identical to the pattern of PCB product with the exception of #11(3,3'-dichlorobiphenyl) that shows a specific pattern. In the biological samples, however, the pattern differs from the product pattern due to metabolic activity. In some water samples, di-chlorinated congeners were found in higher proportions pointing to the influence caused by paint material [3,3'-dichlorobenzidine]. In the environmental samples, air, water and sediment, the pattern sifts from lower to higher chlorinate side respectively. Furthermore, in biological samples, the pattern sifts to higher chlorinated side in the order of clam, fish, and birds. In bird samples, the peak is seen at the hexa-chlorinated congeners similarly as in the human samples such as breast milk² and blood³.

Chlordanes Many POPs involve various isomers and congeners, the fact renders a key for estimation of the origin and kinetics and thus essential for assessing exposure. Chlordanes are constituted mainly of *trans*-chlordane (t-CHL), *cis*-chlordane (c-CHL), *trans*-nonachlor (t-NCL), and *cis*-nonachlor (c-NCL). Oxy-chlordane (OXY), which is a metabolite, is also detected in the environment. Heptachlor [HEP] itself is regulated as an active ingredient in agro-

chemicals. However, heptachlor consist about 10% of the technical chlordane product and some part changes into heptachlor-epoxide [HEPX] that is detected in the environment. The relative

concentrations of these seven congeners are shown in Figure 2 in means with SDs. The figure on top shows the composition of common technical chlordane product.

In the air, although the ratios of *cis*-nonachlor and heptachlor were slightly low, the overall composition was similar to that of the product. The concentration ratio between chlordane and nonachlor also shows are high significance. On the other hand, the origin of oxy-chlordane that consists 10 % is unclear. Chlordane with similar composition as the product was detected in water and sediment. Although the variance is large, it is observed that the most of the heptachlor is transformed into heptachlor-epoxide and resides in this form. In the bivalves investigated, mostly blue mussel, *trans*-chlordane composition was low compared with the sediment. In fish, the tendency was obvious and also the *cis*-chlordane composition lowers, while *trans*-nonachlor and oxy-chlordane go up. Furthermore in birds, *trans*-chlordane almost disappears and *trans*-nonachlor and oxy-chlordane accumulate as the main components.

DDTs, HCHs DDTs, which product contains *p,p'*- and *o,p'*-DDT at 80 and 20 % respectively, tend to includes more DDE in the oxidative environment of air and water and more DDD in the reductive environment of sediment. Bivalves and fish reflect the composition in the sediment. In birds, DDTs are highly metabolized into DDE and accumulates solely in the form of *p,p'*-DDE. For HCHs, the composition was similar to the product in the air, while α -HCH decline and β -HCH increase was observed in water and sediment. Bivalves and fish reflect this composition rate. In birds, however, α - and γ -HCH almost disappear while β -HCH persists.

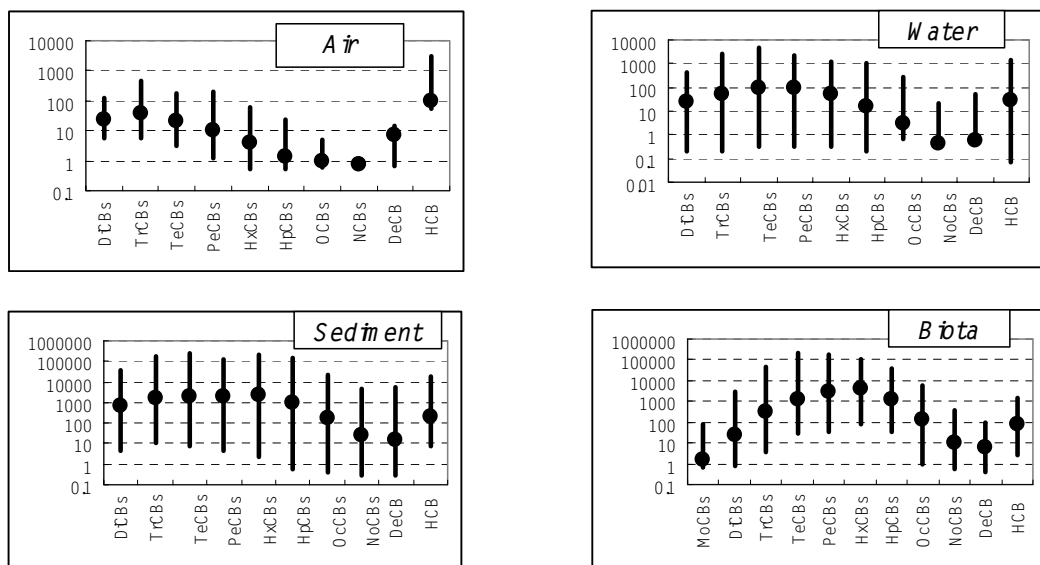


Figure 3: PCB homologue profile and HCB level in air, water, sediment, biota. (Air: pg/m³, Water: pg/L, Sediment: pg-g-dry, Biota: pg/g-wet)

The authors hope to acquire precise information on the origin, kinetics, and trends over time of these compounds in the environment through the adoption of analytical methods with higher sensitivity, resolution and specificity and to contribute to the enforcement of more effective measures. Also for other pollutants, we need to utilize analytical methods with higher sensitivity to ensure the agreement of the convention, that is to achieve fundamental information on the pollutants' "regional/global behavior".

Our new round of POPs monitoring survey has now started to produce valuable information for the elucidation of the conditions of the pollution and the kinetic of the pollutants. Here we presented the results of high frequency data at the average concentration levels, discussed the concentration ratios and composition changes, and reconfirmed the previous founding.

As shown in Figure 1, however, the actual levels of individual POPs are distributed in wide range. In the case of the detection of high levels especially, the through investigations on the source of POPs taking into account the region-specific information such as the data on the use of the product in the area are indispensable.

Acknowledgements

This study was supported by POPs monitoring survey from the Ministry of Environment.

References

1. Suzuki N., Shibata Y., Takazawa Y., Nakano T., Fukushima M., Yoshida Y., Nakajima N., Enomoto Y., Tanabe S. and Morita M. (2004) Organohalogen compounds, in press.
2. Konishi Y., Kuwabara K. and Hori S. (2001) Arch Environ Contam Toxicol 40(4), 571
3. Hirai T., Fujimine Y. and Nakano T. (2003) Organohalogen compounds, 63, 417

LEVELS IN SOIL AND WATER

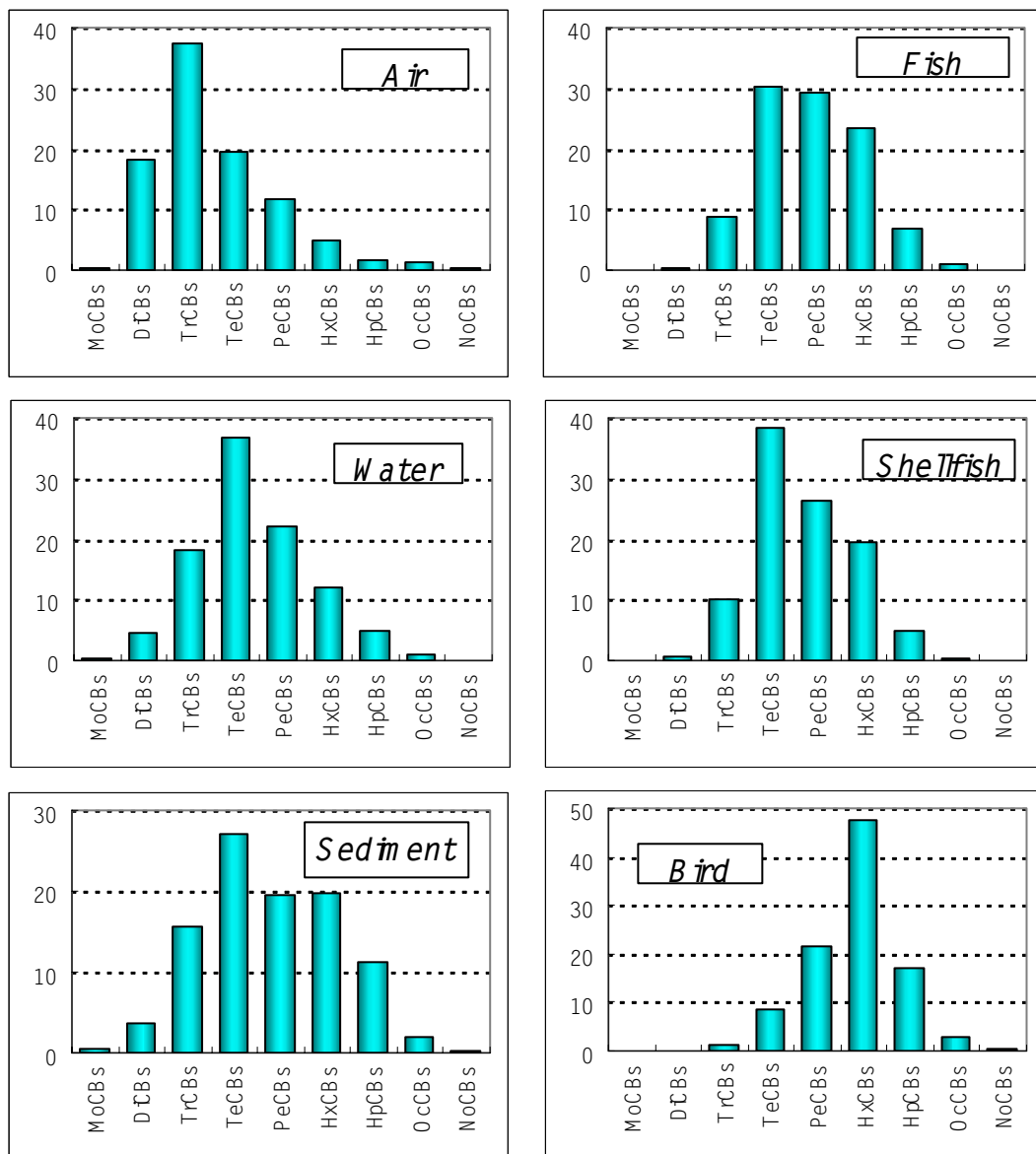


Figure 4 : Homologue profile of PCB in Air, Water, Sediment, Fish, Shellfish and Bird.