

PCDD/Fs, PCBs, HCHs and HCB in Sediments and Soils of Ya-Er Lake Area in China: Results on Residual Levels and Correlation to the Organic Carbon and the Particle Size

W.Z. Wu¹, K.-W. Schramm², B. Henkelmann², Y. Xu¹, Y.Y. Zhang¹ and A. Kettrup²

¹State Key Laboratory of Freshwater Ecology and Biotechnology, Institute of Hydrobiology, Wuhan 430072, P.R. China

²GSF-Forschungszentrum für Umwelt und Gesundheit, Institut für Ökologische Chemie, Ingolstädter Landstr. 1, D-85764 Oberschleißheim, Germany

1. Introduction

PCDD/Fs, PCBs, HCHs and HCB are high lipophilic, chemically stable and easily accumulated in the food chain. For humans the main sources of exposure to these compounds are dairy products, meat, vegetable and fish. Therefore, PCDD/Fs, PCBs, HCHs and HCB may produce a wide spectrum of toxic effects in animals and humans. In the Ya-Er Lake area of China, the chemical plant which produce chloride compounds, have discharged a lot of waste water to contribute significant amount of PCDD/Fs, PCBs, HCHs and HCB burden in the sediment and soil in Ya-Er Lake area. To investigate this question, sediment and soil from this area were sampled and analysed. The organic carbon and particle size of sediments and soils were also measured. The relationship between residual levels and organic carbon and particle size will be discussed.

2. Experimental

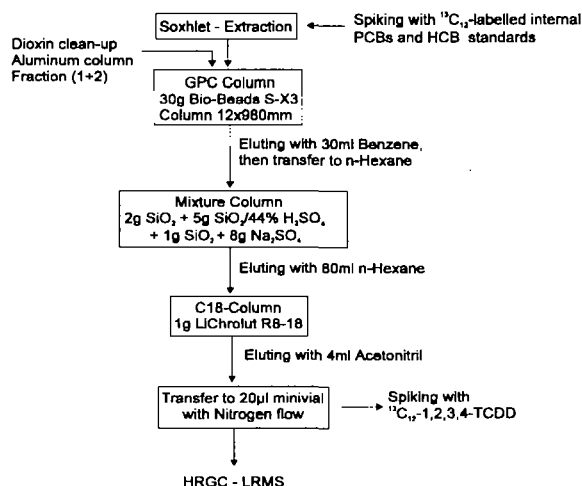


Figure 1 Clean-up procedure of PCBs analysis

Samples were taken from August 1991 to July 1994. The sampling locations for the study are indicated in the figure 1 of the former report²⁾. Afterwards, the samples were transported to the laboratory and freeze dried. The samples were examined for the following compounds: PCDD/Fs, PCBs, HCHs, and HCB.

The clean-up procedures for PCBs and HCB analysis are shown in figure 1. The PCDD/Fs analysis procedures are included in figure 2. The HCHs analysis method was reported in former reports¹⁾.

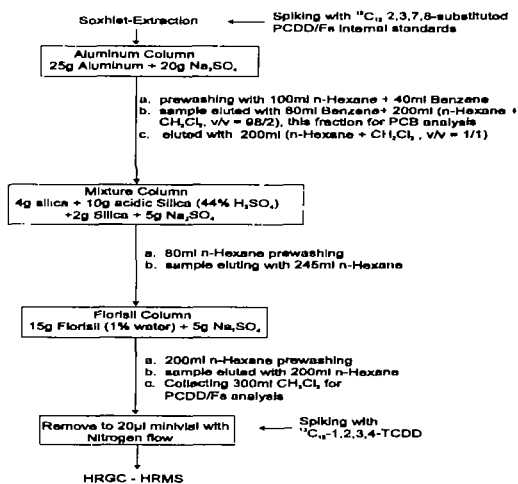


Figure 2 Clean-up procedure of PCDD/Fs analysis

3. Results and Discussion

Sediments and soils collected from the Ya-Er Lake area in China were analysed for PCDD/Fs, PCBs, HCHs and HCB. The concentration and TEQ (calculated using international toxic equivalent factors) of the compounds investigated in this study presented in Table 1. The data indicated three trends. First is the main pollution problems in the Ya-Er Lake area, which was heavily polluted by HCHs and chlorobenzenes, now is dominantly polluted by PCDD/Fs, PCBs and HCB but not HCHs after ban of HCHs production. HCB is a main product from the chemical plant near Ya-Er lake. The HCHs continuously degraded to low concentration. Second is an increase in analytic levels with increasing chlorination for each group of PCDD/Fs and with decreasing chlorination for PCBs congeners. The occurrence of PCDD/Fs and PCBs with relatively high levels of HpCDDs, OCDD and low chlorinated-substituted PCBs is attributed to two factors. First in the Chinese process of pentachlorophenol (PCP) production, PCDD/Fs and PCBs produced as by-products may enter the Ya-Er Lake area following the discharge of waste water. Second, high levels of PCP and chlorinated hydrocarbons may be converted via biological mechanisms to PCDD/Fs and PCBs. Third is decrease in concentrations of PCDD/Fs, PCBs and HCHs with a progression from No.4 to No.6 following the water flow. These pollutants in the soil are in the same levels as sediment nearby. HCB is in the same levels in the soil and sediment at different locations. The vertical distributions of HCH-residues are related to the content of organic carbon and particle size (figure 3).

Table 1 PCDD/Fs, PCBs, HCHs and HCB concentrations in sediments and soils (ng/kg dw)

| | Sediment 1 | Sediment 4 | Sediment 5 | Sediment 6 | Soil 1 | Soil 2 |
|--|------------|------------|------------|------------|--------|--------|
| Sum Tetrachlorinated dibenzo-p-dioxin | 1892 | 0.58 | 0.62 | 6.74 | 0.65 | 0.40 |
| Sum Pentachlorinated dibenzo-p-dioxin | 1836 | 0.05 | 0.23 | 15.5 | n.d. | n.d. |
| Sum Hexachlorinated dibenzo-p-dioxin | 2885 | 1.78 | 16.4 | 56.1 | 0.13 | n.d. |
| Sum Heptachlorinated dibenzo-p-dioxin | 14311 | 11.53 | 59.0 | 145 | 1.08 | 7.73 |
| Octachlorinated dibenzo-p-dioxin | 136592 | 56.7 | 369 | 1116 | 14.6 | 24.4 |
| Sum Tetra- bis Octachlorinated dibenzo-p-dioxin | 157517 | 70.6 | 445 | 1339 | 16.4 | 32.5 |
| 2,3,7,8-Tetrachlorinated dibenzo-p-dioxin | 49.5 | 0.09 | 0.03 | 0.46 | n.d. | n.d. |
| 1,2,3,7,8-Pentachlorinated dibenzo-p-dioxin | 96.2 | 0.01 | 0.23 | 3.87 | n.d. | n.d. |
| 1,2,3,4,7,8-Hexachlorinated dibenzo-p-dioxin | 1199 | n.d. | 1.38 | 8.09 | n.d. | n.d. |
| 1,2,3,6,7,8-Hexachlorinated dibenzo-p-dioxin | 168 | 0.03 | 1.35 | 8.15 | n.d. | n.d. |
| 1,2,3,7,8,9-Hexachlorinated dibenzo-p-dioxin | 95.2 | n.d. | 0.05 | 0.21 | n.d. | n.d. |
| 1,2,3,4,6,7,8-Heptachlorinated dibenzo-p-dioxin | 8130 | 3.79 | 16.8 | 44.6 | 0.49 | 6.78 |
| Sum Tetrachlorinated dibenzofuran | 8834 | 0.89 | 6.00 | 27.8 | 0.90 | 0.74 |
| Sum Pentachlorinated dibenzofuran | 3033 | 0.24 | 2.16 | 8.28 | 0.05 | 0.43 |
| Sum Hexachlorinated dibenzofuran | 1601 | 0.04 | 1.25 | 13.42 | 0.54 | 0.45 |
| Sum Heptachlorinated dibenzofuran | 1557 | 0.12 | 1.45 | 7.59 | 0.01 | 0.03 |
| Octachlorinated dibenzofuran | 4882 | 0.13 | 2.34 | 21.3 | 0.15 | 0.13 |
| Sum Tetra- bis Octachlorinated dibenzofuran | 19909 | 1.43 | 13.2 | 78.4 | 1.64 | 1.77 |
| 2,3,7,8-Tetrachlorinated dibenzofuran | 1448 | 0.10 | 0.21 | 1.62 | 0.17 | n.d. |
| 1,2,3,7,8/1,2,3,4,8-Pentachlorinated dibenzofuran | 665.3 | 0.09 | 1.24 | 6.30 | n.d. | 0.19 |
| 2,3,4,7,8-Pentachlorinated dibenzofuran | 368 | 0.02 | 0.04 | 0.48 | 0.05 | n.d. |
| 1,2,3,4,7,8/1,2,3,4,7,9-Hexachlorinated dibenzofuran | 708 | 0.03 | 0.18 | 2.62 | 0.49 | 0.45 |
| 1,2,3,6,7,8-Hexachlorinated dibenzofuran | 208.7 | 0.01 | 0.14 | 2.30 | n.d. | n.d. |
| 1,2,3,7,8,9-Hexachlorinated dibenzofuran | 25.9 | n.c. | 0.02 | 0.05 | n.d. | n.d. |
| 2,3,4,6,7,8-Hexachlorinated dibenzofuran | 81.0 | n.c. | 0.02 | 0.08 | 0.04 | n.d. |
| 1,2,3,4,6,7,8-Heptachlorinated dibenzofuran | 260 | 0.01 | 1.24 | 5.13 | 0.01 | 0.03 |
| 1,2,3,4,7,8,9-Heptachlorinated dibenzofuran | 239 | n.d. | 0.02 | 0.07 | n.d. | n.d. |
| Sum PCDD and PCDF (Tetra bis Octa) | 177427 | 72.1 | 458 | 1418 | 18.1 | 34.3 |
| TE (nach BGA) | 800 | 0.25 | 1.59 | 6.87 | 0.11 | 0.16 |
| TE (nach NATO/CCMS und 17. BImSchV) | 797 | 0.15 | 1.11 | 6.90 | 0.11 | 0.15 |
| Ballschmitter PCB | | | | | | |
| 2,4,4'-Trichlorobiphenyl | 34666 | 294 | 389 | 379 | 335 | 283 |
| 2,2',5,5'-Tetrachlorobiphenyl | 14252 | 162 | 219 | 218 | 145 | 149 |
| 2,2',4,5,5'-Pentachlorobiphenyl | 2135 | 67.0 | 79.0 | 100 | 87.0 | 84.0 |
| 2,2',3,4,4',5'-Hexachlorobiphenyl | 5181 | 115 | 104 | 123 | 147 | 121 |
| 2,2',4,4',5,5'-Hexachlorobiphenyl | 3882 | 148 | 190 | 156 | 190 | 163 |
| 2,2',3,4,4',5,5'-Heptachlorobiphenyl | 2115 | 47.0 | 39.0 | 52.0 | 63.0 | 40.0 |
| Sum of Ballschmitter PCB (µg/Kg TM) | 5970 | 0.80 | 1.00 | 1.00 | 1.00 | 0.80 |
| Non-ortho PCB | | | | | | |
| 3,3',4,4'-Tetrachlorobiphenyl | 11624 | 46.0 | 107 | 51.0 | 9.00 | n.d. |
| 3,3',4,4',5-Pentachlorobiphenyl | 553 | n.c. | n.d. | n.d. | n.d. | n.d. |
| 3,3',4,4',5,5'-Hexachlorobiphenyl | 135 | n.c. | n.d. | 22.0 | 11.0 | 12.0 |
| Sum of Non-ortho PCB | 12312 | 46.0 | 107 | 73.0 | 20.0 | 12.0 |
| Sum of Mono-ortho PCB | 18078 | 283 | 408 | 435 | 263 | 145 |
| Sum Monochlorobiphenyle | 4685496 | 3511 | 12499 | 3807 | 1634 | 1270 |
| Sum Dichlorobiphenyle | 980218 | 1.57 | 2931 | 1145 | 689 | 666 |
| Sum Trichlorobiphenyle | 134533 | 1872 | 1444 | 2034 | 1613 | 1594 |
| Sum Tetrachlorobiphenyle | 92796 | 2339 | 3571 | 2356 | 2990 | 2442 |
| Sum Pentachlorobiphenyle | 29110 | 325 | 388 | 485 | 432 | 445 |
| Sum Hexachlorobiphenyle | 21963 | 594 | 642 | 669 | 659 | 580 |
| Sum Heptachlorobiphenyle | 11391 | 192 | 103 | 155 | 187 | 152 |
| Sum Octachlorobiphenyle | 5413 | n.d. | n.d. | n.d. | n.d. | n.d. |
| Sum Nonachlorobiphenyle | 9470 | n.d. | n.d. | n.d. | n.d. | n.d. |
| Decachlorobiphenyl | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Sum of PCB: (µg/kg TM) | 5970 | 9.90 | 21.6 | 10.7 | 8.20 | 7.10 |
| TE (Safe 1990) | 196 | 0.75 | 1.48 | 2.04 | 0.89 | 0.76 |
| TE (WHO/PCBS 1994) | 64.1 | 0.03 | 0.06 | 0.25 | 0.12 | 0.13 |
| Alfa-HCH (µg/kg) | 4.96 | 0.95 | 0.90 | 1.96 | 0.35 | 1.55 |
| Beta-HCH (µg/kg) | 12.37 | 1.56 | 1.40 | 2.87 | 0.41 | 2.63 |
| Gamma-HCH (µg/kg) | 0.90 | 0.51 | 0.42 | 1.51 | 0.22 | 0.48 |
| Delta-HCH (µg/kg) | 2.92 | 1.23 | 1.10 | 2.95 | 0.28 | 1.00 |
| Concentration of Hexachlorobenzene: (µg/kg TM) | 57124 | 31487 | 49427 | 41609 | 35410 | 37717 |

n.d.: not detected

The PCDD/Fs and PCBs patterns show very high similarity among all samples between input and output site of Ya-Er Lake, but the concentration ratio of some congeners is slightly different ²⁾. From the history and hydro- geography of Ya-Er Lake area, the pollutants are mainly come from the waste water from the chemical plant. The patterns of these compounds should be equal. This fact can be explained by the different recoveries and activities of biota in the six locations but also by the water flood and deposition of fly ash from the atmosphere.

From the results of HCHs, the vertical profile of the HCHs residue was still the same in the draining channel as inside the lake but the concentrations were higher than those inside the lake ¹⁾. This was caused by the resuspended sediment where the lipophilic HCHs are adsorbed, especially in the case when seasonal flood and storm run off occurred. Thus, suspended particles in waters play a very important role on the fate and transfer of nonionized hydrophobic organic pollutants like HCHs in aquatic environment. This results also can be found for PCDD/Fs and PCBs. This results acquire significance in the fact that the sediment of the Ya-Er Lake may further pollute the agricultural land as well as Yangtze River.

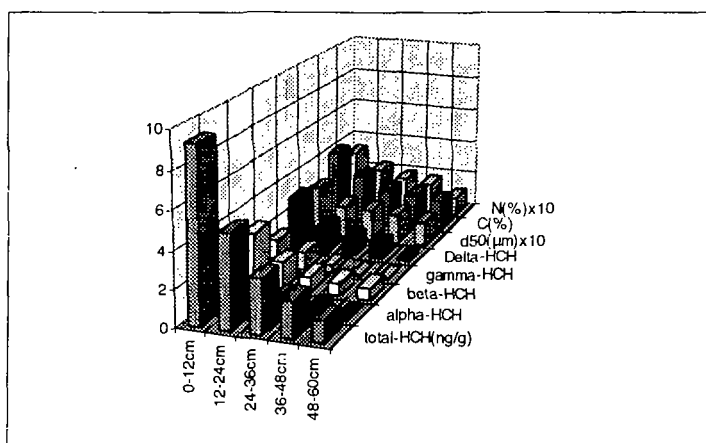


Figure 3 The vertical distributions of HCHs, organic carbon and particle size in sediment

Figure 3 shows the mean particle size (d_{50}) and organic carbon content (C%) for the sediment and soil. The residual levels of HCHs have good correlation to the particle size and the organic carbon. Dissolved organic carbon may assist in the binding of pesticides by having adhesive effect. From figure 3, organic nitrogen also has same vertical pattern as HCH-residues. Large particles may be fewer in number than small particles in the water column, they contribute a greater amount of HCHs to the sediment due to their large mass and more rapid setting rate, and small particles can aggregate forming large particles. The surface sediment has more organic carbon content. The HCHs are mainly residue in the surface sediment. The results for the distribution of PCDD/Fs, PCBs and HCB in the vertical profile of sediment will be reported in the near future.

4. References

- 1). Y. Xu, W.Z. Wu, Y.Y. Zhang, H. Staudacher, A. Kettrup, C.E.W. Steinberg, *Fresenius Envir. Bull.* **3**, 557-562 (1994).
- 2). W.Z. Wu, K.-W. Schramm, B. Henkelmann, Y. Xu, Y.Y. Zhang, A. Yediler, A. Kettrup, Survey on polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in sediments and soils in Ya-Er Lake area, China. *Intern. Environ. Anal. Chem.*, submitted (1995).