

OC PESTICIDES AND PCBs IN SLUDGE AND SEDIMENTS FROM THE GULF OF GDAŃSK AREA

Jerzy Falandysz 1, Katarzyna Szymczyk 1, Masahide Kawano 2, Christoffer Rappe 3

¹University of Gdańsk, 18 Sobieskiego Str., PL 80-952 Gdańsk, Poland

²Ehime University, 3-5-7 Tarumi, Matsuyama, 790 Japan

³Umeå University, S-901 87 Umeå, Sweden

#Present address: University of Warmia and Mazury, Olsztyn, Poland

Introduction

Organochlorine pesticides (OCs) and polychlorinated biphenyls (PCBs) are man-made compounds, which become widespread contaminants and pollutants on a global scale (1). Those substances from many years contaminate the Baltic Sea (2-4). Many of the active ingredients of organochlorine pesticide formulations and their metabolites as well as of the congeners of PCB and PCN are very persistent chemicals in the marine environment, which are toxic, bioaccumulate and biomagnify in the marine food webs (2, 5). Soil and sediment are secondary source of many persistent organochlorines which cycle in the biosphere (6, 7).

The number of studies on occurrence of persistent, toxic and bioaccumulative organic compounds in sludge and sediments in the Baltic south coast region is highly limited (8-11). This paper reports on the concentrations and profiles of many OCs in sludge samples collected in 1999 and sediment samples taken in 1992 from the region of the Gulf of Gdańsk.

Materials and Methods

Sewage sludge samples were collected from the Dębogórze sewage treatment plant (Oczyszczalnia Dębogórze) in the vicinity of the city of Gdynia in spring 1996. Sludge samples were collected separately from two sludge fermentation tanks after primary treatment. One surface sediment sample (0-10 cm) was collected from the Vistula River at the site Kieźmark (near the city of Gdańsk, Voivodeship Pomorskie) from the depth of ~0.5 m and about 2 meters from the shore-line, and one from the depth of 97 m in the Gdańsk Depth (N 54° 43'; E 19° 14') in the Baltic Sea in 1992 (Figure 1). The samples after collection were placed in clean polyethylene bags and deep frozen (-20°C) until analysis.

The analytical method used for the quantification of organochlorine pesticides, PCBs and PCNs have been described elsewhere (12). Briefly, the samples were homogenised and extracted wet in a Soxhlet Dean Strak apparatus with toluene (24 hours) and a mixture of *n*-hexane and acetone (59:41, v/v; 24 hours). The analysis and detection was performed using high resolution gas chromatography/low resolution mass spectrometry (HRGC/LRMS). The MS instrument was a Fison MD 800 operating in the Electron Impact (EI) mode using iron recording (SIR). The GC was a Fisons GC 800 with DB-5 (60 m x 0.32 mm I.D. and 0.25 µm film thickness) column. In the case of organochlorine pesticides quantification was performed against external standard containing, except some of the minor constituents of technical chlordane, all compounds determined in this study and in the case of PCBs one PCB congener for each homologue group. The reported concentrations were corrected for the recovery rates.

AQUATIC ENVIRONMENT

Results and Discussion

DDT and its metabolites, PCBs, HCBz, dieldrin, CHLs and PCNs were quantified in one to all four samples examined (Table 1), while PCBz, TCPM-H/OH, aldrin, isodrin, endrin, endosulfan 1 and 2, and mirex were not detected above the detection limit of the method. To our knowledge reports on

Table 1. Organochlorine pesticides, PCBs and PCNs (ng/g d.w.) in sludge and sediments from the Gdańsk region, Baltic Sea

Compound	Sludge		Sediment	
	Dębogórze 1	Dębogórze 2	Vistula River	Gdańsk Depth
HCHs	ND (<0.5)	ND (<0.5)	ND (<0.1)	ND (<0.1)
PCBz	ND (<0.3)	ND (<0.3)	ND (<0.05)	ND (<0.05)
HCBz	8.6	11	4.7	0.93
DDTs	330	490	77	15
TCPM-H/OH	ND (<1.7)	ND (<1.7)	ND (<0.3)	ND (<0.3)
CHLs	4.0	4.1	0.13	ND (<0.7)*
Dieldrin	8.6	9.9	ND (<0.20)	ND (<0.20)
Aldrin	ND (<0.8)	ND (<0.8)	ND (<0.15)	ND (<0.15)
Endrin	ND (<0.8)	ND (<0.8)	ND (<0.15)	ND (<0.15)
Isodrin	ND (<6.7)	ND (<6.7)	ND (<1.2)	ND (<1.2)
Endosulfan 1, 2	ND (<17)	ND (<17)	ND (<3)	ND (<3)
Mirex	ND (<1.7)	ND (<1.7)	ND (<0.3)	ND (<0.3)
PCBs	650	370	5.6	1.2
PCNs	NA	NA	6.7	NA

ND (not detected); NA (not analysed); *from <0.04 to <0.12 for the main chlordane constituents

concentration of many groups of organochlorine pesticides in sewage sludge from the region of the Gulf of Gdańsk are not available. A recent study has reported the occurrence of PCBs in sludge from the sewage treatment plant in the city of Gdańsk (11). Concentrations of PCBs in dried sludge from the Oczyszczalnia Wschód sewage treatment plant in Gdańsk ranged between 130 and 370 ng/g and there was no significant reduction in load of this compounds after primary treatment in open sludge fermentation tank. In this study concentrations of PCBs in sludge (Table 1) were between 370 and 650 ng/g dry wt., *i.e.* twice that of the sludge from the city of Gdańsk. Polychlorinated biphenyls dominated among organochlorine compounds quantified in sludge samples while DDT and its metabolites dominated in the sediment samples (Table 1). An elevated concentrations of PCBs in sludge when compared to sediments suggest that until the year 1994 not purified wastewater discharged from the Dębogórze sewage treatment plant could be an important local source of PCBs pollution in the Puck Bay. There is no a major differences in profile of chlorobiphenyl congeners between sludge collected from two different sludge fermentation tanks and a large difference for sediment samples. DDTs are next to PCBs as dominating compounds in sludge. The profile of DDTs in sludge samples is very similar and the same can be found for sediments, respectively, but there are large differences between those two matrices with *p,p'*-DDT and *p,p'*-DDE abundant in sediment

A similarity of DDTs profile between sediments from the Vistula River and Gdańsk Depth suggest common origin of those compounds and a dominating role of the river as a source of DDTs washed-out from the soil in the drainage area and further transported/relocated towards to the Gdańsk Depth.

Acknowledgements. The funding for this study was provided by the Japan Society for the Promotion of Science (JSPS), University of Umeå, Umeå, Sweden and Polish State Committee of the Scientific Research (KBN) under grant no.

References

- 1) Wania, F., Mackay, D. (1995) Tracking the distribution of persistent organic pollutants. *Environmental Science and Technology* **30**, A390-A396.
- 2) Bernes, C. (1998) Monitor 16. *Swedish Environmental Protection Agency*. ISBN 91-620-1189-8.
- 3) Falandysz, J., Trzosińska, A., Szefer, P., Warzocha, J., Draganik, B. (2000a) The Baltic Sea: especially southern and eastern regions. In *Seas at The Millenium: An Environmental Evaluation. Vol. I Regional Chapters: Europe, The Americas and West Africa*. C.R.C. Sheppard (editor), Elsevier Science Ltd. 2000, 99-120.
- 4) Ishaq, R. (1999) Fractionation and analysis of chlorinated and non-chlorinated aromatic compounds in biotic and abiotic environmental samples. *Ph. D. Thesis*. Stockholm University, 1999.
- 5) Falandysz, J., Puzyn, T., Szymczyk, K., Kawano, M., Markuszewski, M, Kaliszan, R., Skurski, P., Błażejowski, J., Wakimoto T. (2001) Thermodynamic and physico-chemical descriptors of chloronaphthalenes: an attempt to select features explaining environmental behaviour and specific toxic effects of these compounds. *Polish Journal of Environmental Studies* **10**, in press.
- 6) Quensen, J.F., Mueller, S.A., Jain, M.K., Tiedje, J.M. (1998) Reductive dechlorination of DDE to DDMU in marine sediment microcosmos. *Science* **280**, 722-724.
- 7) Bidleman, T.F., Jantunen, L.M.M., Wiberg, K., Harner, T., Brice, K.A., Su, K., Falconer, R-L., Leone, A.D., Aigner, E.J., Parkhurst, W.J. (1998) *Environmental Science and Technology* **32**, 1546-1548.
- 8) Falandysz, J. (1992) Organochlorine pesticides and polychlorinated biphenyls in surface sandy sediments of the Puck Bay (in Polish). *Bromatologia i Chemia Toksykologiczna* **25**, 387-390.
- 9) Kawano, N., Falandysz, J., Tsuji, S., Kitamura, S., Wakimoto, T. (1997) Extractable organic halogen (EOX) and man-made organochlorine compounds in soils and sediments from the Northern Poland (in Japanese). *Journal of Environmental Chemistry* **7**, 7-13.
- 10) Kawano, M., Falandysz, J., Brudnowska, B., Wakimoto, T. (1998) Organochlorine residues in freshwater sediments in Poland. *Organohalogen Compounds* **39**, 331-335.
- 11) Kannan, K., Kober, J.L., Khim, J.S., Szymczyk, K., Falandysz, J., Giesy, J.P. (2001) Polychlorinated Biphenyls, Polycyclic Aromatic Hydrocarbons and Alkylphenols in Sediments from the Odra River and its tributaries, Poland. *Environmental Chemistry and Toxicology*. Submitted.
- 12) Strandberg, B. (1998) The use of semipermeable membrane devices in studies of concentrations, distribution and fate of organochlorine compounds in the environment. *Ph. D. Thesis*. Umeå University, Umeå.