Organohalogen Compounds 70 (2008) 2001-2004

CONTAMINATION OF CZECH RIVERS AND DREISSENA POLYMORPHA WITH PCBs FROM THE POINT OF VIEW OF THE ORTHO SIDE CHLORINATED CONGENERS

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Introduction

Persistent organic compounds play significant role for their impacts on the human health and environment especially being present in water. Monitoring and assessment of persistent organic compounds (POPs) seems to be a very complex scope. Whereas analytical procedures passed through past 20 years by remarkable development, sampling analytic procedures are still of increasing importance and progress. In parallel to conventional active sampling (grab sampling) passive sampling methods were found, based on biotic and abiotic accumulation of POPs. A new integral passive sampling technology for POPs reflecting aquatic exposure is based on the use of semipermeable membrane device (SPMD) for concentration of hydrophobic, lipophilic and toxic organic contaminats. SPMD where triolein has been selected as a standard sequestrant filled in lay flat low density polyethylene membrane exhibits good results for sequestering of non polar compounds[1]. Nowadays, various organisms are routinely used for assessing waterborne bio-available chemicals. The concentration found after their exposure has certain variability due to their characteristics (anatomy, physiology, behaviour, migration, etc.). Dreissena polymorpha was used for exposure and comparison to SPMDs. PCBs were widely applied in the industry, e.g. as coolants and lubricants in transformers, dielectric fluids in capacitors and heat-transfer media, hydraulic fluids and as additives mainly into paints. Their industrial production started in the year 1929 under various trade names (e.g. Aroclor A1016 analogous to Delor 103; Aroclor A1260 analogous to Delor 106). More than 11000 tons of Delors was produced and applied in the former Czechoslovakia within the period of 1959 to 1984. This is the reason that some parts of the Czech Republic are still contaminated with PCB.

Materials and methods

Dreissena Polymorpha used for sampling was collected in sand-pit with very clean water. Small shells were placed in polypropylene cages (100 pieces/cage) and fixed at the same float as SPMDs. Used SPMDs have a standard dimension (2.5x91.4cm, filled by 1 ml of triolein) and they were purchased from Exposmeter AB. SPMDs were exposed for 26–30 days in May and in June 2001, Dreissena Polymorpha was exposed for both two months in 2001. SPMD dialysates and Dreissena extracts were analysed by GC/MS/MS using isotope dilution and internal standard[2].

Results and discussion

The water of rivers Morava and Elbe were analysed for 95 PCB congeners by using the SPMD sampling method in May and June 2001. The sampling places are as follows: the river Morava - Lanžhot (near the town Břeclav upstream the confluence with the river Dyje); the river Elbe - Hřensko (between the town Děčín and the outflow to Germany).

The percentage of the chlorinated biphenyl homologues is presented in Figure 1. From these results it is evident that distribution of PCB homologues in the rivers differs significantly. In the river Elbe congeners of tri- and tetra-chlorinated biphenyls (CBs) are highly prevailing, however, for the case of the river Morava main contaminating components are highly chlorinated penta- to hepta-CBs. From our analyses it is evident that Delor 103 (Aroclor A1016) contains mainly the mono-ortho and 2,2´-di-ortho-chlorinated biphenyls. The highly

chlorinated Delor 106 (Aroclor A1260) contains not only the highly chlorinated tri-ortho-chlorinated congeners but also the 2,6-di-ortho-chlorinated and mono-ortho-chlorinated biphenyls. In the Figure 2 comparison of non-ortho- to tetra-ortho-chlorinated biphenyls distribution in the rivers Elbe and Morava with Delors 103 and 106 is presented. From results we can conclude that the river Elbe is contaminated first of all by Delor 103, whereas the river Morava by Delor 106. The river Morava flows through Uherské Hradiště where production of paints was realised. The total contamination of the rivers Morava and Elbe with polychlorinated biphenyls corresponds to the value of 1302 pg PCBs/l and 6475 pg PCBs/l, respectively, which means that contamination of the river Elbe as compared with river Morava is approx. 5 times higher.

The effects of contamination level in the rivers Elbe and Morava on the accumulation of the polychlorinated biphenyls in the whole dry mass of Dreissena polymorpha after two months exposure in rivers is presented in the Figure 3. From the results it is evident that the concentrations of non-ortho and mono-ortho-chlorinated PCBs in Dreissena polymorpha are considerably lower compared with the content in rivers, while the 2,2´-di-ortho-chlorinated PCBs are practically as the same. Dominating accumulation of tri-ortho chlorinated biphenyls as well as the pronounced accumulation of 2,6-di-ortho- and tetra-ortho-chlorinated PCBs has been found. There are different opinions for understanding the reasons of these accumulation phenomena. From our point of view very high thermodynamic stability and rigid structure of compounds mentioned above might be the possible and serious reason for accumulation in the biota. From the Table 1 it is obvious that values of dihedral angles for tri-ortho and tetra-ortho biphenyls are of about 88 to 90^{o} which means that the aromatic rings are perpendicular to each other. However, for certain structures of 2,6-di-ortho-chlorinated biphenyls the perpendicular structure might exist as well. It is well known that the aromatic rings of biphenyls which contain three or four and even also two large groups in the ortho sides of biphenyl structures cannot rotate about the central bond because of the steric hindrance[5]. From the Table 1 it is evident that for PCB congeners with perpendicular aromatic rings the internal energy barriers of rotation are extremely high and correspond to hundreds kJ/mol, which is more than two orders of magnitude higher value in comparison with PCB congeners with non-ortho- and mono-ortho-chlorinated structures. These facts might explain the above mentioned proposals. Highly different properties of chlorinated biphenyls especially with respect to their structures and thermodynamic stabilities might be a serious reason for different health effects for humans. Polychlorinated biphenyls elicit a diverse spectrum of toxic responses which were even stated for Delors 103 and 106[6].

Acknowledgments
This work was supported by The Grant Agency of Czech Republic under Grant No. 104/07/1212. Authors acknowledge the financial support of CHMI´s bioaccumulation monitoring by the Ministry of Environment of the Czech Republic.

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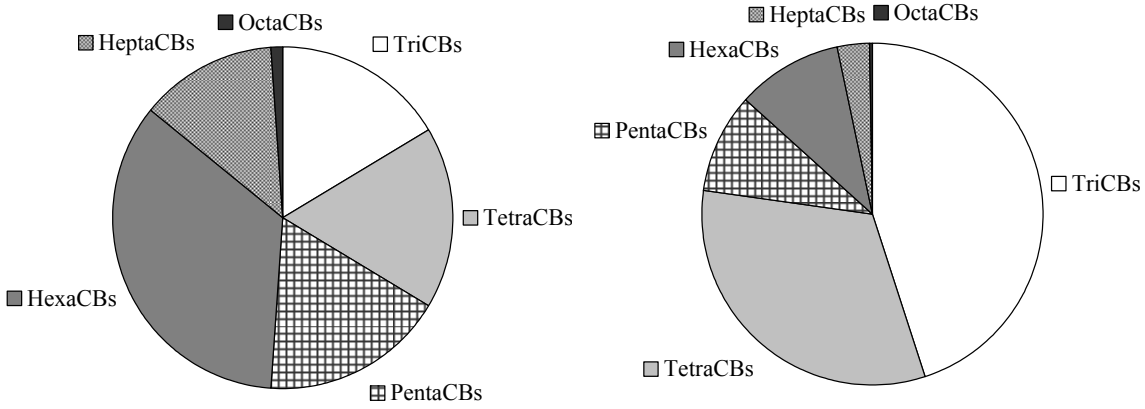
Table 1 The dihedral angles and internal barriers of rotation for different ortho-side chlorinated PCBs

Ortho positions	ω, dihedral angles[3] (°)	Internal barriers of rotation[4] (kJ/mol)
non-ortho-	38-48	8.33-9.79
mono-ortho-	51-57	28.5-34.9
2,2´-di-ortho-	67-89	60.2-73.9
2,6-di-ortho-	77-90 (prevailing 89-90)	66.4-190
tri-ortho-	88-90	177-224
tetra-ortho-	89-90	373-483

Figure 1 The percentage of the chlorinated biphenyl homologues in the rivers (tri- to deca-chlorinated biphenyls)



The river Morava The river Elbe

Figure 2 The ortho side chlorinated PCB congeners in the rivers as compared with congeners in Delor 103 and Delor 106 (non-ortho to tetra-ortho biphenyls)

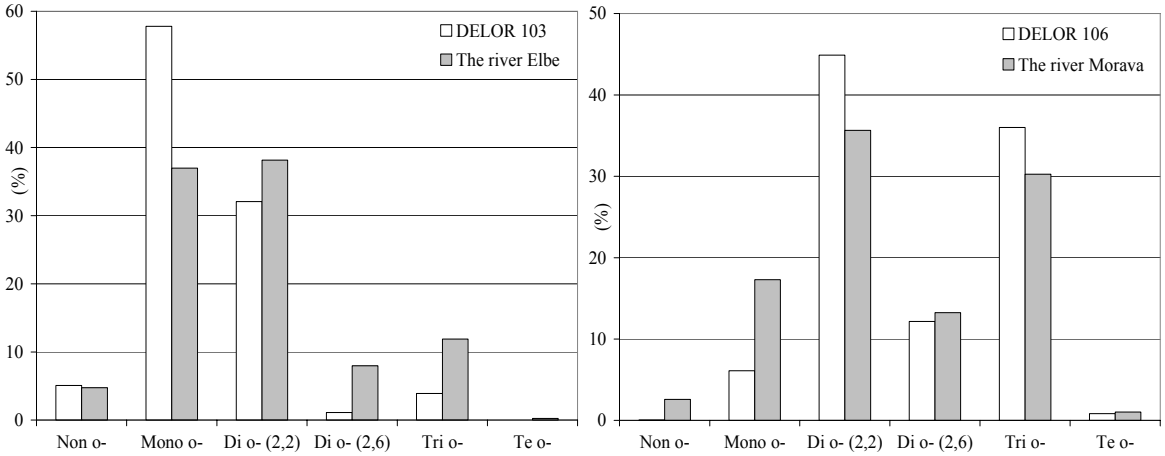


Figure 3 The ortho side chlorinated PCB congeners in the rivers as compared with contamination in Dreissena Polymorpha (non-ortho to tetra-ortho biphenyls)