LEVELS OF PBDEs AND PCBs IN SEDIMENTS AND SEWAGE SLUDGES COLLECTED IN SEVERAL REGIONS OF THE CZECH REPUBLIC

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Introduction

Polychlorinated biphenyls (PCBs) and brominated flame retardants (BFRs) such as polybrominated diphenyl ethers (PBDEs) represent the most noted classes of persistent organic pollutants (POPs) possess a potential to bioaccumulate through the food web. [1] In wastewater treatment plants (WTPs), significant portion of PBDEs and PCBs in the influent may survive the water treatment and accumulated in the sludge generated from processes due to their hydrophobic nature (i.e. low solubility in water) and potentially slow degradation kinetics. These environmental pollutants can move into the sediments due to groundwater when contaminated sewage sludges is landfilled and land-applied. [2]

While monitoring of PCBs in various, both abiotic and biotic matrices, was initiated as early as in 70th last century, the ubiquitous occurrence of PBDEs was recognized approx. twenty years later. With regard to increasing concentration in human blood and breast milk, the production of commercial penta- and octa-BDEs technical mixtures was banned in the EU in 2004. On this account, only those products based on deca-BDE are currently permitted. However, due to their former wide use in many goods, a release of lower chlorinated PBDE congeners into the human environment undoubtedly still continues. [3,4]

The objective of the present study was to get more information on the levels and congener profiles of structurally similar POPs - PBDEs and PCBs - in sediments and sewage sludges collected in selected sampling sites of the Czech Republic. The generated data are needed for identification of potential emission sources and management of potential problem.

Experimental

Sediments and sewage sludges (1 kg) were collected during autumn 2007 in 15 sampling sites located at several Czech rivers. Prior to storage, samples were dried for 12 h at 40°C and then thoroughly homogenized. 20 g of representative sample aliquot were mixed with 20 g of anhydrous sodium sulphate and extracted in a Soxhlet extractor for 8 h using 170 ml dichloromethane (DCM). The extract was rotary-evaporated, re-dissolved in 10 ml cyclohexane:ethylacetate (1:1, *v/v*) solvent mixture and then cleaned up using gel permeation chromatography, GPC (Bio Beads S-X3). The eluate fraction containing both PBDEs and PCBs was concentrated on a rotary evaporator and re-dissolved in 500 µl isooctane. To remove remaining matrix coextracts, several drops of sulphuric acid were added. A determination of PBDEs was performed on an Agilent 6890 gas chromatograph coupled with a mass spectrometer (Agilent 5975 MSD) operated in a negative chemical ionization mode. 1µl of concentrated extract was injected into a DB-XLB (30 m x 250 µm i.d. x 0.1 µm film thickness) capillary column and a DB-XLB (15 m x 250 µm i.d. x 0.1 µm film thickness) capillary column in case of BDE 209. The indicator PCB congeners were quantified using an HP 5890 gas chromatograph equipped with two electron capture detectors (ECDs) on two capillary columns with different polarity DB-5 and DB-17 (60 m x 250 µm i.d. x 0.25 µm film thickness). GC method used for analysis of target compounds has been previously described in detail by Hajšlová et al. [5].

Results and discussion

The overview of PBDE levels in river sediments and sewage sludges from wastewater treatment plants (WTPs) examined within this study is shown in **Table I**. The latter matrix was distinctly more contaminated, containing, almost without any exception, a whole set of target PBDE congeners. It was noted that the pollution pattern of sludges was markedly different among the sampled WTPs, what documents the diversity of PBDE mixture uses. BDE 209 was the most abundant congener in all samples; its concentration in sludge collected in locality Ostrava was as high as 1709 ng/g dw what was several times higher in comparison with the sum of lower brominated congeners. No correlations between deca-BDE and other PBDEs were found. Excluding BDE 209 the sum of other congeners was highest in locality Hradec Králové. It was assumed that this was due to emissions from local industry producing TV electronics. Relatively high contamination by these, recently banned PBDEs, was found in sludges collected in wastewater treatment plants localized in another industrialized area – Ústí nad Labem. The levels of lower brominated PBDEs in river sediments were in many sampling sites below or very close to method detection limits (LODs). In line with extensive contamination of sewage sludge from WTP by BDE 209 found in Ostrava, also sediments contained relatively high concentrations of this congener.

Similar congener profiles were obtained in both types of test matrices, with the following order: BDE 209 >> BDE 47 ~ BDE 99 >> BDE 100 > BDE 153 ~ BDE 154 ~ BDE 183. On the other hand, congeners No. 28, 66 and 85 were less abundant in evaluated environmental compartments. When comparing the contamination in individual sampling localities, the highest concentrations of sum of PBDEs (BDE 209 not included) were found in sewage sludge from Hradec Králové (320.6 ng/g dw). The typical PBDE congeners profile is illustrated in **Figure 1**.

The data generated in this study were also compared to similar studies conducted in various other countries. For instance, de Boer et al. (2003) reported comparable levels of PBDEs in sewage sludges from Netherlands [6]. Generally, the levels of PBDEs in sludges from the Czech Republic were lower than those reported in studies conducted in the North America, for example Hale et al. (2001) measured levels ranging from 1100 to 2290 ng/g in sludge from four different regions in the United States [7].

Table 1 Major PBDEs in sewage sludges and sediments collected in various localities, the Czech Republic, 2007

	Location	PBDE congeners (ng/g dw)							Σ PBDEs *)	BDE 209
		47	49	99	100	153	154	183		
Sewage sludge	Český Krumlov	2.4	0.2	1.8	0.5	0.3	0.3	0.4	6.0	118.8
	České Budějovice	20.34	2.01	20.13	5.02	1.53	1.47	3.10	53.6	373.3
	Klatovy	9.5	2.0	7.9	2.3	1.1	1.0	1.7	25.5	27.0
	Plzeň	17.5	2.4	20.3	5.3	1.9	1.7	3.0	52.2	48.5
	Praha	30.0	1.0	24.0	7.1	< 0.1	1.9	1.1	65.2	195.2
	Hradec Králové	128.5	11.0	134.5	28.2	8.0	7.6	2.9	320.6	629.1
	Pardubice	10.0	0.7	11.1	2.8	1.6	1.4	2.2	29.9	131.5
	Teplice	34.5	2.5	41.9	8.6	3.0	2.7	3.0	96.1	119.2
	Ústí n/Labem	34.9	2.5	43.5	37.6	3.0	2.5	1.9	126.0	28.1
	Jihlava	20.5	1.1	25.3	5.3	2.0	1.7	2.3	58.2	982.7
	Brno – Modřice	26.3	2.1	32.9	6.9	2.7	2.2	4.2	77.2	559.3
	Uherské Hradiště	8.7	0.5	9.1	2.3	1.5	0.8	1.3	24.1	213.2
	Olomouc	5.1	0.4	6.1	1.6	0.8	0.6	1.1	15.6	201.8
	Opava	28.2	1.1	29.4	8.3	3.1	2.0	13.6	85.8	283.5
	Ostrava	9.8	0.5	9.4	2.4	1.0	0.8	2.2	26.1	1709.4
Sediment	Klatovy	0.2	0.1	0.3	0.1	0.1	0.1	0.3	1.2	24.8
	Plzeň	< 0.1	< 0.1	< 0.1	< 0.1	0.1	1.7	< 0.1	52.2	< 0.1
	Praha – left bank	0.1	0.1	0.2	0.2	< 0.1	< 0.1	0.1	0.6	< 1.4
	Praha – right bank	0.1	< 0.1	0.2	0.2	0.8	< 0.1	4.2	5.5	14.6
	Hradec Králové	0.7	0.1	0.6	0.2	0.3	0.1	0.1	2.1	130.6
	Pardubice	0.4	0.2	0.5	0.2	0.2	0.2	< 0.1	1.7	7.4
	Teplice	0.2	0.1	0.2	0.1	0.1	0.1	0.1	0.9	< 1.4
	Brno – Modřice	1.1	0.2	1.0	0.2	0.2	0.2	0.5	3.4	22.7
	Uherské Hradiště	0.1	0.1	0.2	0.1	0.1	0.1	0.1	0.8	< 1.4
	Olomouc	0.1	< 0.1	0.2	0.1	0.1	0.1	0.1	0.7	10.7
	Opava	0.5	0.1	0.5	0.2	0.2	0.1	0.3	1.8	19.5
	Ostrava – upstream WTP	2.3	< 0.1	1.0	0.3	0.2	0.2	0.7	4.7	276.4
	Ostrava – downstream WTP	0.6	0.1	0.4	0.1	0.1	< 0.1	0.2	1.4	2.5
	Klatovy – upstream WTP	0.2	0.1	0.3	0.1	0.1	0.1	0.1	1.0	< 1.4

*) Σ PBDEs does not include congener No. 209
WTP – wastewater treatment plant

Sewage sludge **Sediment**

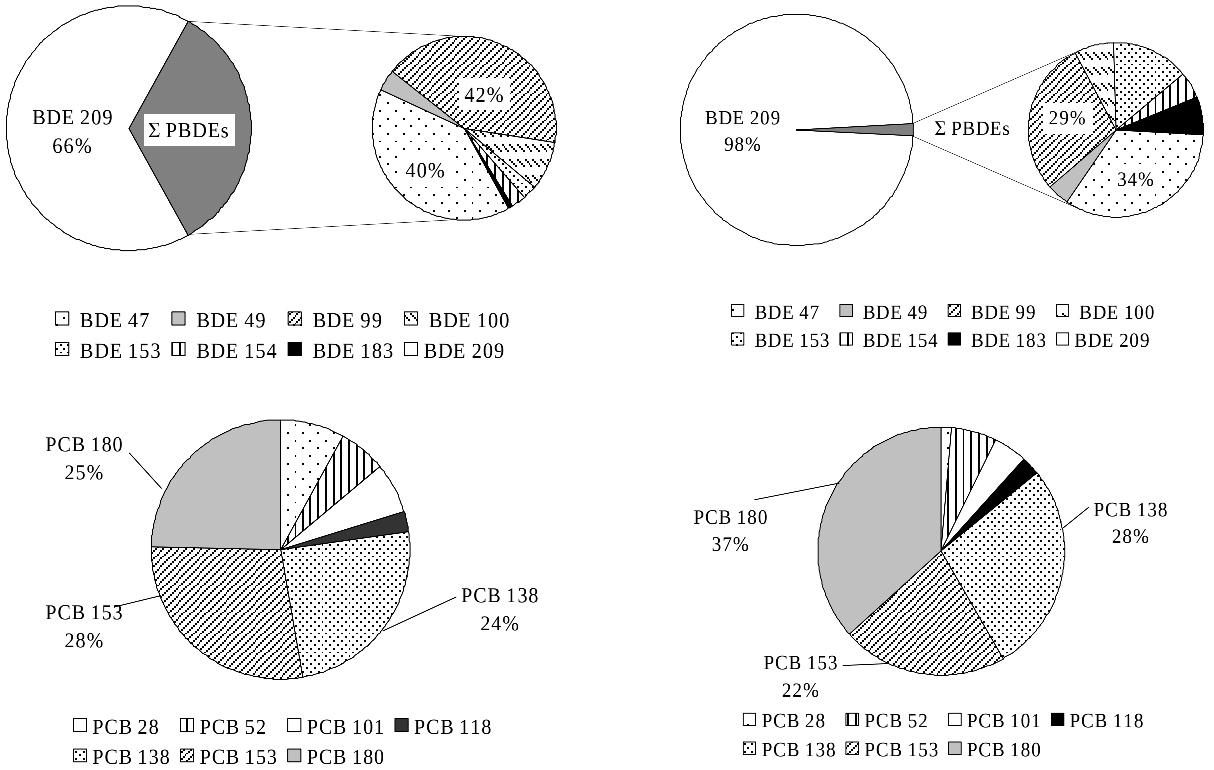

Figure 1 PBDE and PCB congeners profile in sewage sludge and sediment from Hradec Králové

Levels of sum of indicator PCBs in river sediments and sewage sludges ranged from 1.5 to 157.2 ng/g dw and from 26.8 to 108.1 ng/g dw, respectively. **Table 2** shows the concentrations of individual indicator PCB congeners in both examined matrices. Regarding the congeners profile, the most abundant were higher chlorinated PCBs, their relative concentrations were as follows: PCB 153 ~ PCB 138 > PCB 180; the lower chlorinated species were present only in trace amounts. Among the monitored localities, the most polluted were the sewage sludges from Ostrava and Uherské Hradiště, while the highest pollution of sediments was observed in Pardubice and Prague (a right bank of the Vltava River). The sediment sample from Pardubice was the only exception in the PCB pattern. A distinct dominance of lower chlorinated PCB 28 and 52 was measured in the sediment; this is probably due to a use of different type of PCB technical mixture based on these lower chlorinated congeners in this area.

To the best of our knowledge, this is the first study in which the levels and congener profiles of PBDEs were monitored together with PCBs in sediments and sewage sludges collected from various locations in the Czech Republic. The important role of wastewater treatment plants was documented in this way: while only low levels of PBDEs were found in river sediments, sewage sludges were significantly more contaminated. On account of association with sewage sludges, their penetration from emission sources into the aquatic ecosystem did not occur in a greater extent. To get more information on the time or seasonal contamination trends, follow-up studies will be realized in a close future.

Table 2 Concentration (ng/g dw) of PCBs in sewage sludge and sediments from Czech Republic

	Location	PCB congeners (ng/g dw)							Σ PCBs
		28	52	101	118	138	153	180	
Sewage sludge	Český Krumlov	0.4	2.9	2.9	1.7	6.8	6.3	5.8	26.8
	České Budějovice	0.6	1.3	1.4	1.3	10.7	8.5	9.5	33.4
	Klatovy	1.9	2.9	4.1	2.6	20.3	23.6	19.7	75.2
	Plzeň	1.9	1.2	1.6	1.1	7.3	8.6	7.0	28.8
	Praha	3.2	2.4	2.7	5.7	3.2	12.1	0.8	30.0
	Hradec Králové	4.0	2.9	3.3	1.3	12.2	14.0	12.4	50.0
	Pardubice	5.8	9.3	17.3	1.5	7.4	9.4	6.6	57.2
	Teplice	3.3	1.8	3.5	5.3	19.5	17.3	17.8	68.4
	Ústí n/Labem	4.3	4.0	7.1	11.8	19.2	20.8	20.8	88.0
	Jihlava	3.5	1.5	1.7	1.3	9.5	7.8	9.2	34.6
	Brno - Modřice	4.1	1.9	7.3	1.4	14.4	17.9	11.8	58.8
	Uherské Hradiště	3.1	6.5	5.3	8.0	26.4	30.7	28.0	108.1
	Olomouc	2.1	1.5	7.1	1.2	15.9	17.6	16.1	61.4
	Opava	3.4	5.2	5.4	1.8	19.3	22.1	19.6	76.8
	Ostrava	9.9	14.9	2.1	1.4	19.7	28.1	30.3	106.4
Sediment	Klatovy	0.3	0.8	0.9	0.7	2.7	2.2	2.0	9.6
	Plzeň	0.3	0.3	0.4	0.3	0.2	0.2	0.4	2.1
	Praha – left bank	1.8	0.8	7.3	2.8	26.6	29.3	37.3	105.9
	Praha – right bank	3.8	2.9	13.5	7.7	46.0	44.6	40.5	158.9
	Hradec Králové	0.3	1.1	0.8	0.5	5.0	4.0	6.7	18.3
	Pardubice	53.9	51.0	9.4	3.4	11.8	15.1	12.6	157.2
	Teplice	0.2	0.9	0.7	0.4	2.2	2.1	1.6	8.1
	Brno – Modřice	1.9	1.2	3.7	2.5	16.4	13.8	12.4	52.0
	Uherské Hradiště	0.4	0.9	1.4	0.6	5.9	6.9	6.0	22.1
	Olomouc	0.4	0.6	1.5	0.9	8.2	7.1	6.6	25.3
	Opava	0.7	0.4	0.5	0.3	9.8	3.8	3.4	18.8
	Ostrava – upstream WTP	4.2	6.7	5.0	3.2	31.0	18.7	13.7	82.6
	Ostrava – downstream WTP	1.3	1.5	0.5	0.7	3.7	6.4	1.7	15.9
	Klatovy – upstream WTP	0.4	1.1	1.4	0.8	4.1	3.5	2.1	13.3

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