PBDES AND HBCD IN SEWAGE SLUDGE AND RIVER SEDIMENTS IN THE CZECH REPUBLIC: A 3-YEAR SURVEY (2006–2008)

Stavelova M [1], Pulkrabova J [2], Hradkova P [2], Kalachova K [2], Zlamalikova J [2], Stiborova H [2], Poustka J [2], Kovar M [1], Mackova M [2], Demnerova K [2], Hajslova J [2]

[1]Earth Tech CZ, Ltd., Prague, Czech Republic; [2]Institute of Chemical Technology, Prague, Czech Republic;

Abstract

During a 3-year survey (2006–2008) 15 monitoring points of WWTP sludge and 13 monitoring points of river sediments were regularly investigated in October and November each year within the Czech Republic (CR) locations. Target brominated flame retardants (BFRs) includes polybrominated diphenyl ethers (PBDE congeners 28, 47, 49, 66, 85, 99, 100, 153, 154, 183, and 209) and hexabromocyclodecane (HBCD). The obtained mean values of stabilized WWTP sludge for the most abundant congeners BDE 209, BDE 47, BDE 99 and HBCD in 2006 were 255.7, 30.7, 29.8 and 12.2 μg/kg dw, respectively. The major changes were detected in 2008 in content of BDE 209 (decrease of mean value to 54.4 μg/kg dw) and in content of HBCD (increase mean value to 173.8 μg/kg dw) in comparison to 2006. The mean value of river sediments shows almost 97% decreasing of total content BFRs in sludge to compare years 2006 and 2008. Generally, BDE 209 decreased from 19.1 to < 1.2 μg/kg dw. HBCD content in median value still was not detected in river sediments in 2008 but some notice about its potential increasing is seen in average value and in maximal content. This study will be continued till 2010. These trends are expected in connection with new law-restrictions of PBDEs and usage of alternative flame retardant mixtures. Our data are comparable with results published in other studies.

Introduction

BFRs are monitored in the CR within one section of the national project BIOBROM. The aim of our group is to investigate the BFRs levels in the Czech ecosystem in years 2006–2010. We have examined river sediments, WWTP sludge, human adipose tissue from liposuction, human breast milk and indoor dust. The monitoring of WWTP sludge and sediments take place annually; other sample types are tested consecutively during the project. Target BFRs includes polybrominated diphenyl ethers (PBDE congeners 28, 47, 49, 66, 85, 99, 100, 153, 154, 183, and 209) and hexabromocyclodecane (HBCD).

Material and methods

Investigated WWTPs cover all territory of the Czech Republic and belongs to the big municipal WWTPs with the loading over 30 000 PE. 3-year study (2006–2008) includes 15 WWTP sludge and 13 river sediments sampled regularly in October and November. The stabilized sludge (approximately 200 g) was collected after the belt press or centrifuge or filter press from 10 portions, homogenized, placed to the glass jar and in cooling box transported to the lab. The only one up-stream river sediment sampling point was placed approx. 200–300 m up to outflow of the WWTP, down-stream river sediments were collected approx. 100–300 m down to the WWTP outflow. The stratified sample of river sediments were taken from the first layer (0–0.5 m) of the sediment by the stainless core sampler from 5 portions and homogenized. About 200 g of sediment sample was placed into the glass jar and transported in cooling box to the laboratory.

These samples were analyzed using Soxhlet extraction, gel permeation chromatography (GPC) and gas chromatography (GC) utilizing mass spectrometry detector with negative chemical ionization (MS/NCI). Analyses were realized at the Institute of Chemical Technology, Prague, CR.

Fig 1: Monitoring points of WWTP sludge and river sediments in the Czech Republic

Results and Discussion

Results of annual monitoring of 15 WWTP sludge are presented in Figure 2. Sum BDE 10 include congeners 28, 47, 49, 66, 85, 99, 100, 153, 154, 183.

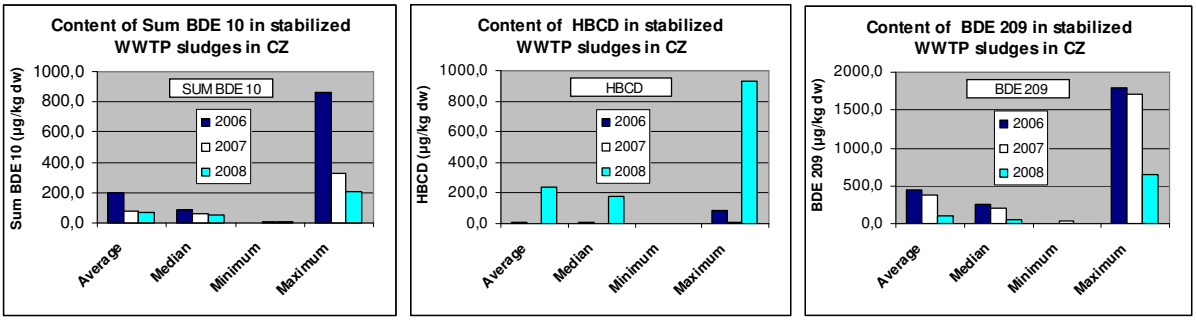


Figure 2: BFRs content in WWTP sludge, annual monitoring

Table I: BFRs content in WWTP sludge, annual monitoring, median, n=15

Stabilized WWTP Sludges 2006–2008, median, n=15, µg/kg dw						
	BDE 47	BDE 99	BDE 100	Other BDE	BDE 209	HBCD
2006	29.8	30.7	7.4	11.8	255.7	12.2
2007	20.4	22.2	5.3	9.6	207.5	3.0
2008	20.6	18.6	3.9	6.4	54.4	173.8

Other BDE= low content BDE: (28, 49, 66, 85, 153, 154, 183)

The results of stabilized WWTP sludge (median values, see Fig. 2 and Table I) show decreasing trend (approx. 30%) of total content of BFRs in samples collected in 2008 as compared to those reported in the fish year of this survey(2006). The significant changes were detected in 2008, especially in content of BDE 209 (drop from aprox. 75% to 20% of total measured BFRs content) and in HBCD levels (increase from approx. 2% to 60% of

total measured BFRs content). Other abundant BDE 47 and BDE 99 kept almost the same contribution of total amount of BFRs – both 7–8%.

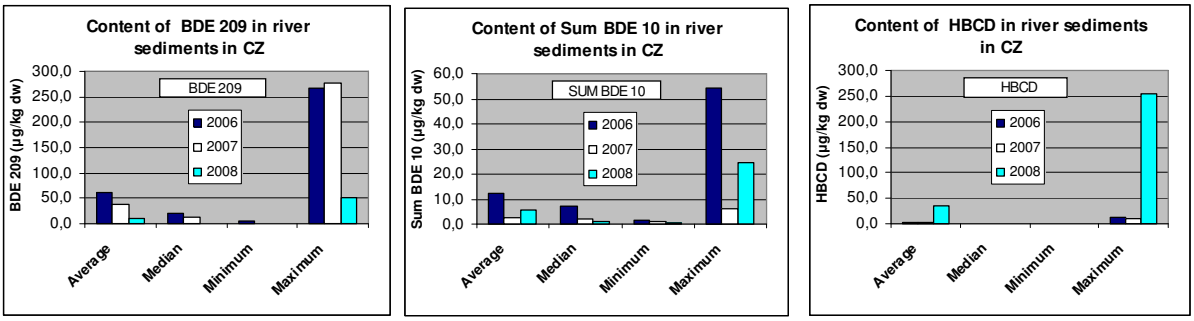


Figure 3: BFRs content in downstream sediments, annual monitoring
Sum BDE 10 includes congeners 28, 47, 49, 66, 85, 99, 100, 153, 154, 183.

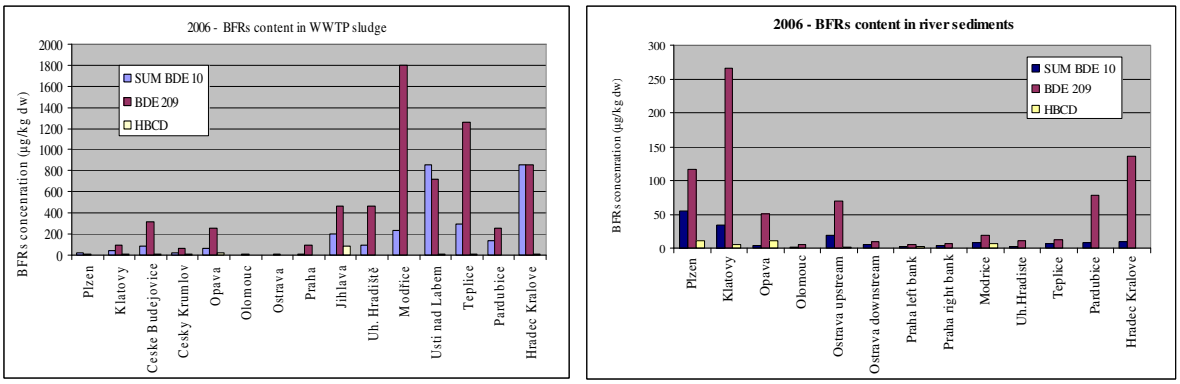
Table II: BFRs content in downstream river sediments, annual monitoring, median, n=13

Downstream river sediments 2006–2008, median, n=13, µg/kg dw						
	BDE 47	BDE 99	BDE 100	Other BDE	BDE 209	HBCD
2006	3.1	1.6	0.4	0.9	19.1	< 0.8
2007	0.4	0.4	0.2	0.8	12.7	< 0.8
2008	0.4	0.3	< 0.1	< 0.1	< 1.2	< 0.8

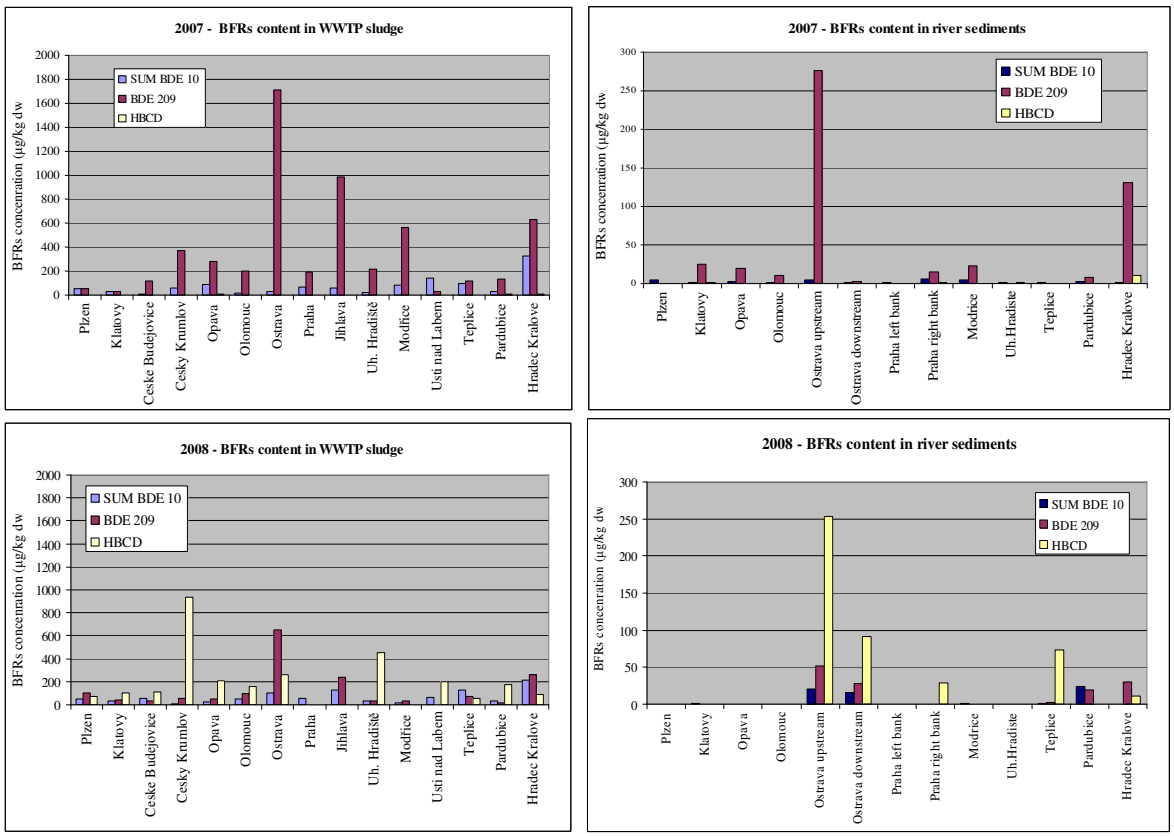
Other BDE= low content BDE: (28, 49, 66, 85, 153, 154, 183)

The BFR results in river sediments collected downstream from WWTPs (median values, see Fig. 3 and Table II show almost 97% decrease of the total content of BFRs in sludge in the comparison years 2006 and 2008. The major changes were detected namely in the levels of BDE 209 (decrease from approx. 75% to less than 4%). However, HBCD was not detected in all examined localities; some increase can be seen in mean value and in maximum content. A specific development of BFRs concentration on all monitoring points for WWTP sludge and river sediments is evident from the following Fig. 4.

Figure 4: Specific development of BFRs concentration on specific monitoring points for WWTP sludge and river sediments.



(Sum BDE 10 includes congeners 28, 47, 49, 66, 85, 99, 100, 153, 154, 183).



(Sum BDE 10 includes congeners 28, 47, 49, 66, 85, 99, 100, 153, 154, 183).

Following Table III for sewage sludge and Fig. 5 for sediments present the comparison of our data with similar studies conducted in other countries worldwide. The content of PBDEs in sludge in the CR is comparable to levels reported in Germany, Spain and China and concentrations of BDE 209 in sediments (the most abundant congener from all investigated BFRs in sediments) correspond to findings from other EU countries and China. The highest concentrations of BFRs in sludge and sediments were published in studies from the U.S.

Table III: PBDEs in WWTP sludge within the world (µg/kg dw)

PBDEs in WWTP sludge within the world				
Country	Range of Sum PBDEs including BDE 209	Published	Author	No. of Samples
	µg/kg dw			
Czech Republic	7.7–2663	2006	Pulkrabova	n=15
Czech Republic	33.7–2039	2007	Pulkrabova	n=15
Czech Republic	5.2–862	2008	Pulkrabova	n=15
Spain	197–1185	2007	Eljaraat	N/A
Germany	231-993	2004	Hamm	n=8
Germany	109.6–2505	2007	Knoth	n=11
USA	730–24900	2001	La Guardia	n=10
USA	1414–5545	2003	Kolic	n=12
USA	1700–3500	2004	Kolic	n=5
Australia	5–4230	2008	Clarcke	n=16
China	6.2–1166	2007	Wang	n=31

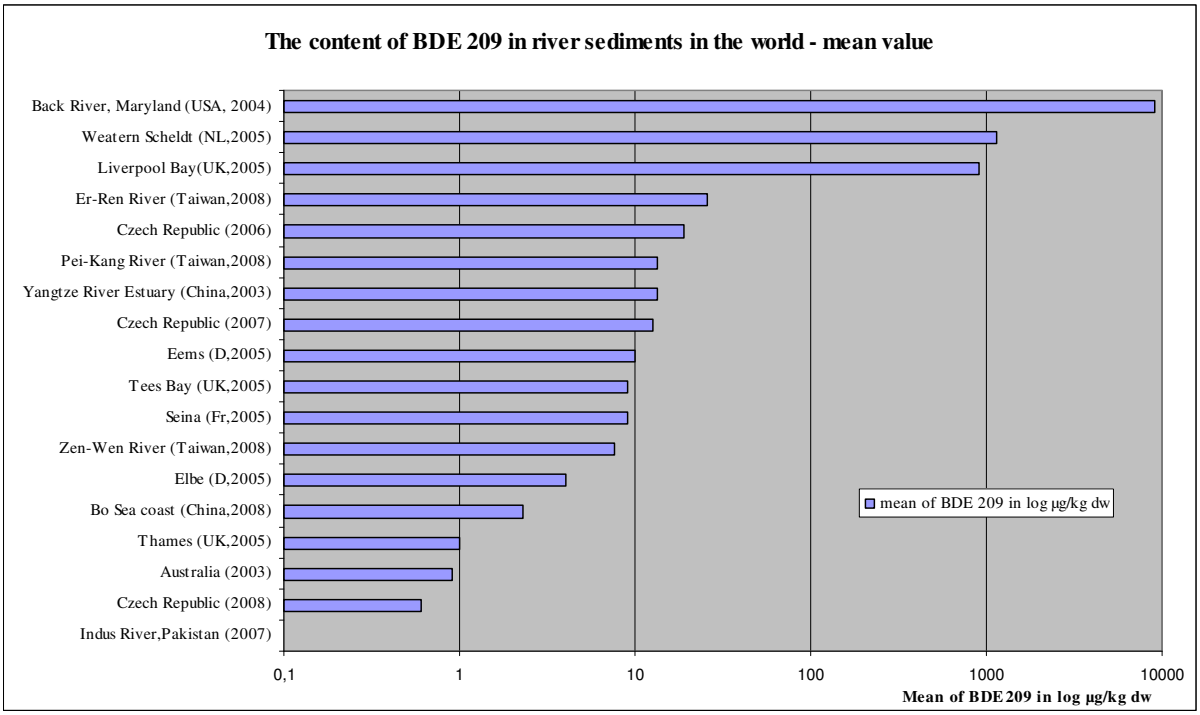


Figure 5: Occurrence of BDE 209 in sediments within the world

Conclusion

Presented data from 2006–2008 from regular autumns monitoring of BFRs content within the Czech Republic from 15 WWTP sludge and 13 river sediments monitoring points, respectively, indicate decreasing trends in PBDEs concentration and slightly increasing trend in HBCD content. This study will continue till 2010. These trends are expected in connection with new law-restrictions of PBDEs and usage of alternative flame retardant mixtures. Our data are comparable with results published in other studies.

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