CONTRIBUTION OF BFRS AND OTHER CONTAMINANTS TO TOXICITY PROFILES OF THE CZECH RIVER SEDIMENTS AND SEWAGE SLUDGE

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Introduction

While monitoring of environmental pollutants, such as polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), polycyclic aromatic hydrocarbons (PAHs) and heavy metals, in various 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 and the usage of deca-BDE is currently under the discussion. However, due to their former wide use in many goods, a release of lower brominated PBDE congeners into the human environment undoubtedly still continues. [1,2]

Residues of these pollutants when released into the environment are adsorbed rapidly onto the solid particles and then readily accumulated in the organic fraction of soils, sediments and sewage sludge [3,4]. The presence of brominated flame retardants (BFRs) in the Czech aquatic environment has been already documented in previous studies [5,6].

Even though sewage sludge is considered to be one of the main stocks of persistent organic pollutants (POPs) only s studies have been conducted in Europe[3] until now on their contamination by BFRs. Since sludge is applied in many countries on an agricultural land, potential contamination of terrestric food chains by these hazardous chemicals is of a high concern. Monitoring must also pay attention on the origin of sludge as the levels of organic contamination may significantly vary when for example comparing municipal sewage sludge (mostly originated from households) with sludge of industrial origin or sludge from storm- and run-off waters. The objective of waste water treatment is to prevent large quantities of substances to reach and impact the environment in high doses and concentrations.

The main aim of the present study was to get more information on the levels and congener profiles of structurally similar POPs – PBDEs, PCBs, OCPs and also PAHs – in sediments and sewage sludge collected in selected sampling sites of the Czech Republic. The generated data are needed for identification of potential emission sources and management of potential problems. Correlations of obtained data with 3 different ecotoxicity tests were also assessed.

Experimental

Sediments and sewage sludge were collected during the autumn 2007 in 15 sampling sites located at several Czech rivers.

Analysis of contaminants

Prior to storage, samples were dried for 12 hrs at 40°C and then thoroughly homogenized. 20 g of representative sample aliquot were mixed with 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 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 target analytes was concentrated on a rotary evaporator and re-dissolved in isooctane in case of halogenated contaminants and in acetonitrile in case of PAHs. Determination of PBDEs was performed on gas chromatography coupled to mass spectrometry (GC-MS) in a negative chemical ionization mode (NCI), PCBs and OCPs were determined by gas chromatography with electron capture detector (GC-ECD) and PAHs by liquid chromatography coupled to fluorescence detector (LC-FLD).

Ecotoxicological analyses

A measurement of the ecotoxicity was performed using 3 bioassays: (*i*) inhibition of the root growth using the seeds of the lettuce (*Lactuca sativa* L. var. capitata L., SAFIR; SEMO s.r.o.), direct contact test, modified version ISO 11269-1, 1993, (*ii*) inhibition of the root growth using the seeds of the lettuce (*Lactuca sativa* L. var. capitata L., SAFIR; SEMO s.r.o.), test using water extracts, modified version of guideline of Ministry of the Environment of the Czech Republic (339/1997) and (*iii*) bioluminescence assay using bacteria Vibrio fischeri, CSN EN ISO 11348-2.

Results and discussion

Within this study, altogether 15 localities were selected for the monitoring of contamination of the aquatic ecosystem of the Czech Republic by BFRs, such as polybrominated diphenylethers (PBDEs) and hexabromocyclododecane (HBCD). Besides this investigation, also other group of environmental contaminants including PCBs, OCPs (such as e.g. DDT and HCB), PAHs and heavy metals were also measured. In each locality both sewage sludge and sediments collected downstream from the sewage treatment plant outfall were analysed.

The overview of all groups of target contaminants in river sediments and sewage sludge examined in our project is shown in **Table I**. Ubiquitous occurrence of BFRs in examined matrices confirmed existence of various emission sources of BFRs in the Czech aquatic environment. No distinct trend or geographical distribution in BFRs levels in sediment and sludge in 15 sampling localities from the different region of the Czech Republic were found. In most localities sewage sludge were significantly more highly contaminated compared to sediments, documenting that they are the main emissions sources. The PBDE congener patterns in examined samples were dominated by the deca-BDE (No. 209), this congener formed between 28 and 95% of the total PBDE contamination. Other relatively highly abundant congeners were BDE 47, BDE 99, BDE 100 and BDE 183. Only traces of BDE 28, BDE 49, BDE 66 and BDE 85 were detected in some samples. No correlations between deca-BDE and other PBDEs were found. Excluding BDE 209 the sum of other PBDE congeners was highest in locality Hradec Kralove. It was assumed that this was due to emissions from local sources.

Table I: Concentrations of target groups of contaminants in sediment and sewage sludge, aggregated data (µg/kg dry weight halogenated contaminants, mg/kg dry weight PAHs and heavy metals), and ecotoxicity tests results (inhibition, %)

	Sediment		**Sewage sludge**	
	mean	**min–max**	**mean**	**min– max**
Dry mass (%)	59.7	42.8–75.4	25.2	12.9–31.7
TOC (%)	2.9	0.6–5.9	27.3	23.1–37.3
BDE 209	51.5	5.3–265.9	445.3	7.3–1803.1
Σ 10 PBDEs	12.4	0.4–54.3	191.8	0.5–859.1
HBCD	5.8	0.2–11.6	17.2	0.6–126.4
Σ PCBs	91.1	nd–467.1	65.7	19.7–119.4
HCB	9.5	0.8–79.6	9.5	1.0–21.4
g-HCH	1.2	0.3–6.2	0.9	0.4–2.0
Σ DDTs	35.4	0.1–106.7	69.2	nd–145.5
Σ 12 PAHs	27.6	0.2–210.7	10.1	1.4–46.1
Hg	0.6	0.08–1.5	8.0	0.8–66.1
As	20.1	8.0–57.9	32.9	nd–55.0
Cd	3.5	0.5–12.4	3.8	1.4–8.1
Pb	53.4	23.6–151.0	73.7	16.0–229.0
Zn	261.1	55.0–720.0	1,182.1	252.0–2,240.0
Root growth inhibition (contact test)	56.3	29.2–79.9	98.0	76.3–100.0
Root growth inhibition (test using water extracts)	-9.5	-17.2–3.2	78.5	34.9–100.0
Bioluminescence assay using bacteria *Vibrio fischeri*	32.8	-24.3–93.4	50.0	22.0–81.9

In all samples not only levels of groups of contaminants mentioned above, bud also toxicity profiles using three different types of ecotoxicity test: (*i*) root growth inhibition (contact test), (*ii*) root growth inhibition (test using water extracts) and (*iii*) bioluminescence assay using bacteria *Vibrio fischeri* were monitored, see **Table I**. For the detailed comparison, two highly contaminated localities (Hradec Králové and Brno), especially by BFRs (the main objective of BIOBROM project) were compared, see **Figure 1-3.** **Figure 1** documented results of ecotoxicity tests, slight differences between individual tests and also between two tested matrices are shown here.

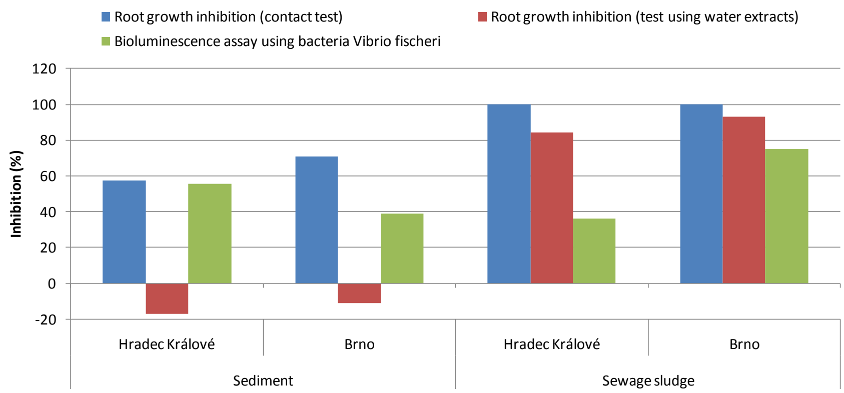


Figure 1: Ecotoxicity of sewage sludge and sediment from localities Hradec Králové and Brno using three different toxicity tests

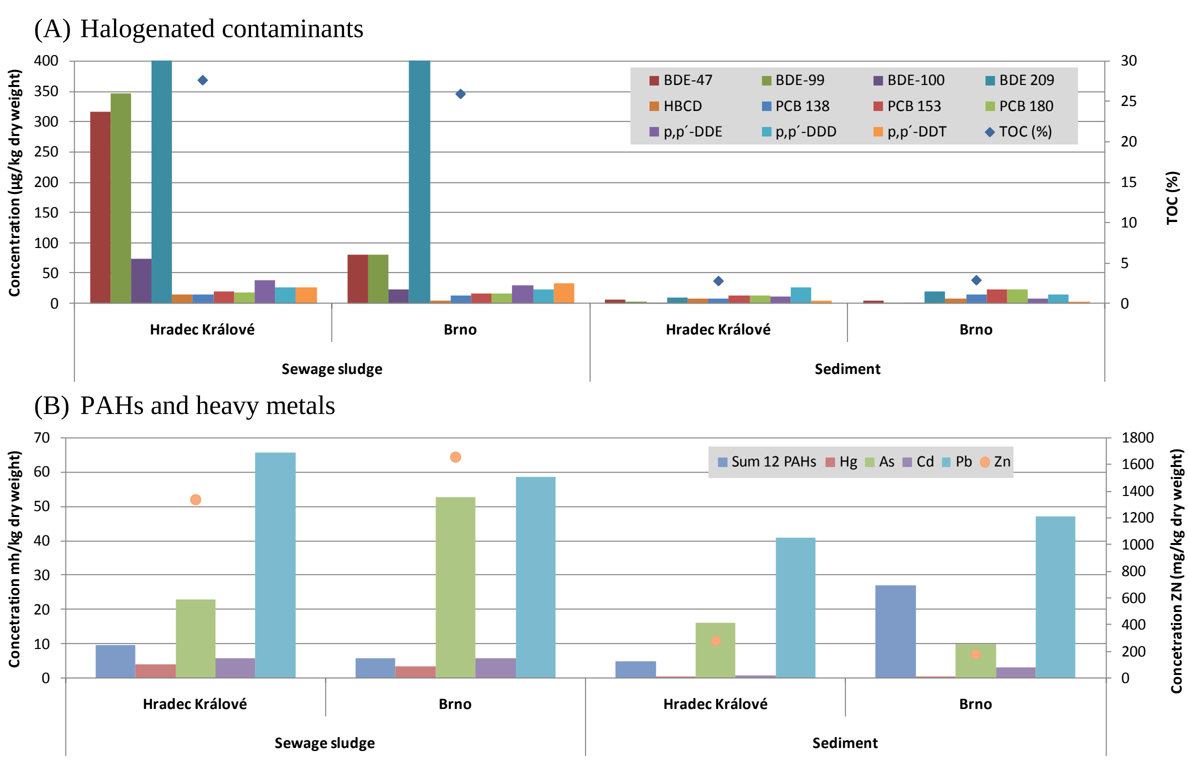
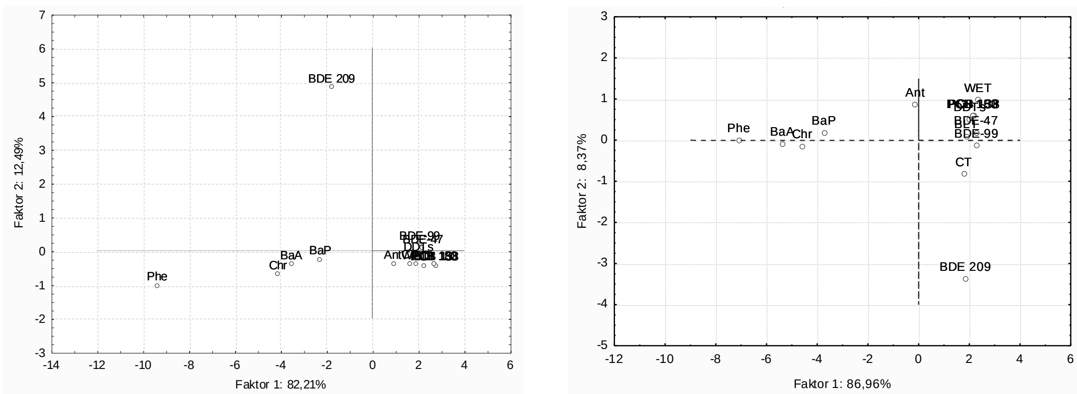


Figure 2: Concentrations of different groups of contaminants in sediment and sewage sludge from locality Hradec Kralove and Brno

As documented in Table 1 and also Figure 2, sewage sludge is much higher contaminated matrix as compared to river sediment, especially in case of brominated pollutants. These two selected localities also largely differ in congener profiles, what could be caused by various pollution sources. The contamination levels of individual groups of pollutants in sewage sludge were in following order: heavy metal > PAHs > PBDEs > PCBs ~ DDTs > HBCD ~ HCH ~ HCB, in river sediment, concentration of all target groups were comparable.



(A) (B)

Figure 3: Results of PCA of date concerning sewage sludge (A) and sediments (B)
Note: CT – contact test, WET – water extract test, BT – bioluminescence test

Principal components analysis (PCA, using STATISTICA 9.0 software) was used to get an overview of the total data set and to obtain information on possible correlations between tested parameters. As documented on **Figure 3** no significant separation/correlation ecotoxicological test and levels of contaminants in sediments and sewage sludge was found within this study.

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