

# Brominated Flame Retardants in River Sediments and Sewage Sludges Collected in the Czech Republic

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**Introduction.** Brominated flame retardants (BFRs), such as polybrominated biphenyl ethers (PBDEs) and hexabromocyclododecane (HBCD), are widely used industrial chemicals added to various materials important in manufacture of electronic equipment, upholstered furniture, construction materials, textiles etc. to inhibit or even suppress the combustion process<sup>1</sup>. The widespread presence of BFRs in various environmental compartments is a consequence of both their broad application area and physico-chemical properties such resistance to (bio)degradation and high lipophilicity. Residues of these persistent organic pollutants (POPs) when released into the environment are adsorbed rapidly onto solid particles and then accumulated readily in the organic fraction of soils, sediments and sewage sludges<sup>1,2</sup>. The presence of BFRs in the Czech aquatic environment has been already documented in previous studies<sup>3</sup>. Similarly to other halogenated aromatic POPs, BFRs are transferred into biota including humans.

Although sewage sludges are considered to be one of the main sinks for persistent organic pollutants (POPs), until now, only few studies have been conducted in Europe<sup>2</sup> on their contamination by BFRs. Since in many countries, sludges are applied on an agricultural land, potential contamination of terrestrial food chains by these hazardous chemicals is of high concern.

The aim of presented study was to find relationship between contamination of sewage sludges and sediments collected downstream of sewage treatment plants (STPs). For analysis, gas chromatography coupled to mass spectrometric detector operated in negative ionization mode (GC/MS-NCI) was used. Novel analytical technique represented by comprehensive orthogonal gas chromatography coupled to time-of-flight mass spectrometry (GCxGC/TOF-MS) was also employed to demonstration its potential. In addition to BFRs, various groups of halogenated and other contaminants were identified by non-target screening enabled by unique features of this innovative technique.

**Material and Methods.** For the purpose of this pilot study, sediments and sewage sludges were collected from 8, 6 resp. sampling sites in the Czech Republic during autumn 2006. Samples of sediments were collected downstream of sewage treatment plants (STPs) - suspected sources of brominated flame retardants compounds. No sediments were available in the localities České Budějovice and Český Krumlov.

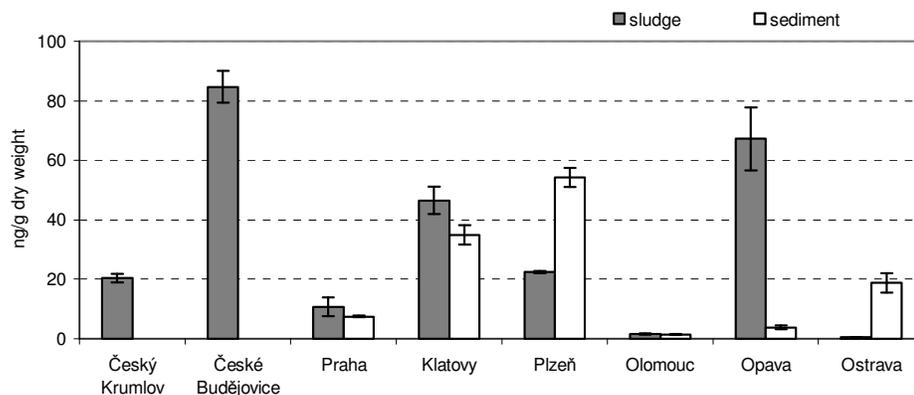
Sample preparation procedure was fully automated and started with pressurised liquid extraction (PLE) employing hexane-acetone (1:1, v/v) solvent mixture under static conditions (15 Mpa, 100°C) for 5 min. Dionex ASE 300 Accelerated Solvent Extractor (Dionex, CA, USA) was used for this purpose. The crude extract was carefully evaporated by rotary vacuum evaporator at 40°C and sample was dissolved in cyclohexane-ethylacetate mixture (1:1, v/v) that was used as a mobile phase in gel permeation chromatography (GPC) employing Bio Beads S-X3 column for separation of interfering co-extracts. Agilent 6890 (Agilent, USA) gas chromatograph equipped with a single quadrupole mass analyser Agilent 5975 XL operated in negative chemical ionization mode (GC/MS-NCI) and DB-XLB capillary was employed for routine analyses of PBDEs and HBCD.

GCxGC-TOF MS Pegasus 4D (LECO, USA) system consisted of an Agilent 6890N gas chromatograph equipped with a high-speed time-of-flight mass spectrometer LECO Pegasus III was used for obtaining a comprehensive information on the whole spectrum of halogenated POPs occurring in respective samples

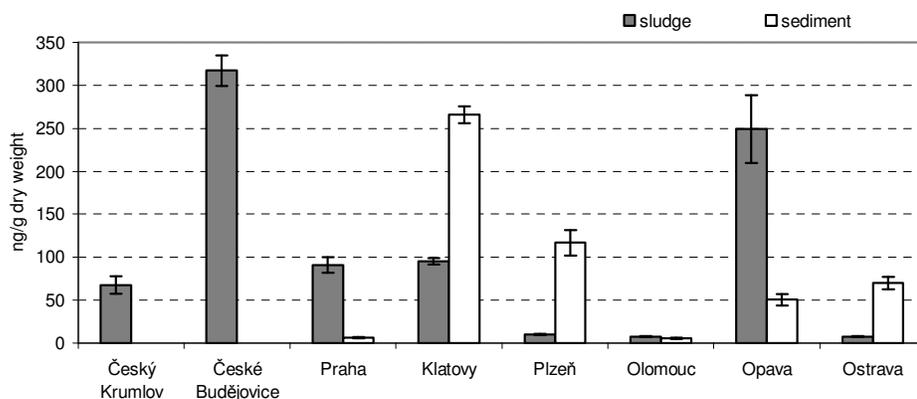
**Results and Discussion.** Ubiquitous occurrence of BFRs in examined matrices confirmed existence of various emission sources of BFRs in Czech aquatic environment. Distinct trend or geographical distribution in comparison of BFRs levels in sediment and sludge in sampling localities was not found.

In most localities sewage sludges were more contaminated as compared to sediments, what documents they are the main source emissions source. The results obtained for all monitored localities are illustrated in Fig. 1 A-C.

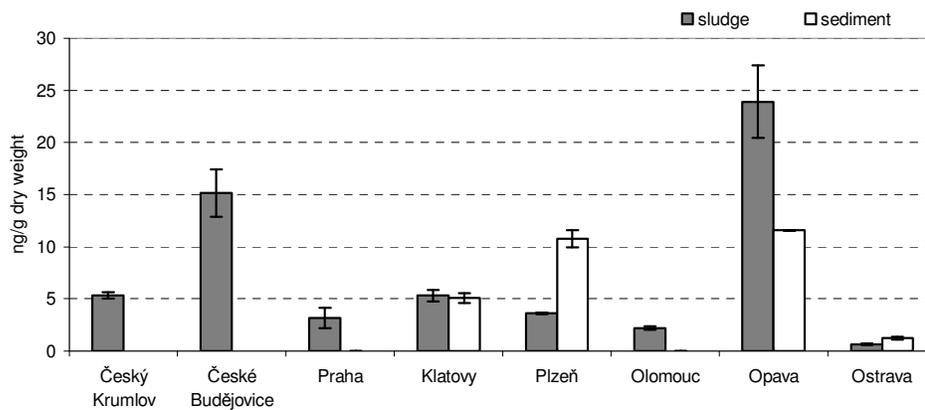
A) PBDEs (sum of 10 congeners)



B) BDE 209

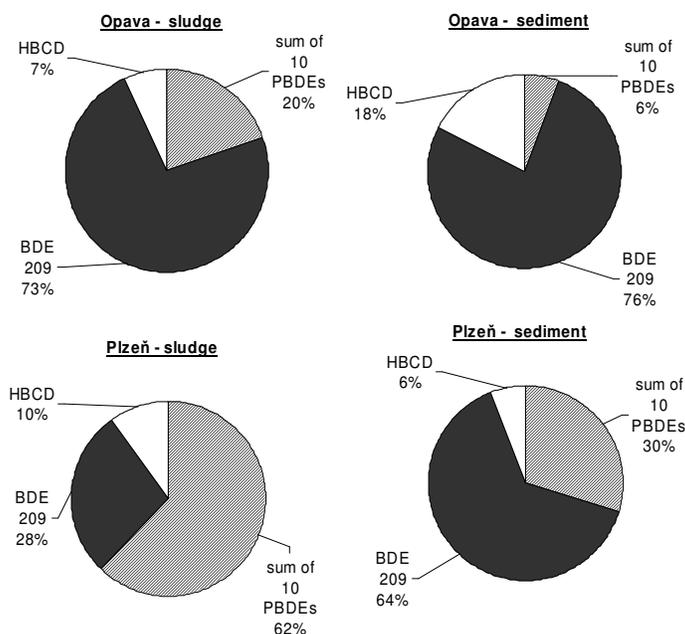


C) HBCD



**Figure 1:** Levels of BFRs (ng/g dry weight) in sediments and sewage sludges examined in this study (sediments were not available in the upper part of Vltava river, sampling sites České Budějovice and Český Krumlov)

The PBDE congeners patterns were dominated by the deca-BDE (No. 209), in examined samples, this congener constituted 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 congeners BDE 28, BDE 49, BDE 66 and BDE 85 were detected in some samples.



**Figure 2:** Comparison of relative contribution of individual BFRs groups in sludges and sediments from two different localities

The diversity of pollution sources is illustrated in Fig. 2. For instance, in sampling site Opava, the sewage sludge was more contaminated as compared to river sediment, however, the pattern of individual BFR groups contribution was practically identical. On the other hand, in Plzeň, the sludge was less contaminated than sediment and BFRs pattern was distinctly different - contribution of BDE 209 was only 28% in sludge while 64 % in sediment. Additional source of pollution of aquatic environment or intensive BDE 209 degradation may be the reason for the above phenomenon found in this sampling locality. Generally, the levels of BFRs in sediments and sewage sludges were consistent with reported data for similar matrices examined for PBDEs e.g. in United Kingdom, Netherlands and Spain<sup>4,5,6</sup>.

Besides of BFRs, many other halogenated POPs were present in purified sludge and sediment extracts, see Fig. 3. Recently introduced GCxGC/TOF MS technique enabled their simultaneous identification/quantification hence provided more comprehensive information on pollution of particular sampling sites. The challenging nature of this approach was clearly demonstrated.

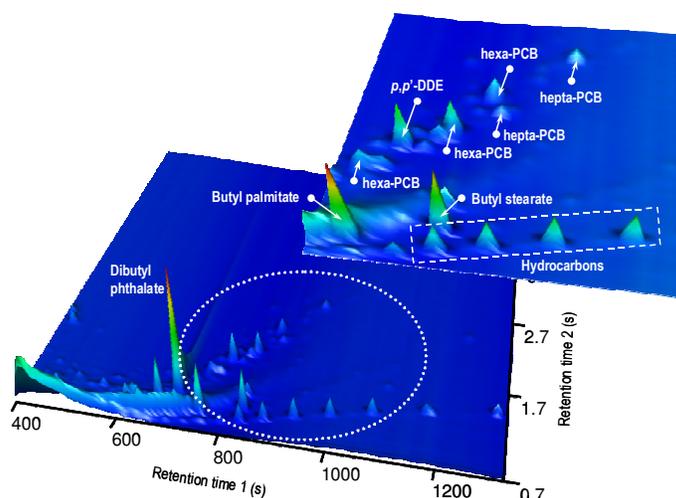


Figure 3: GCxGC–TOF MS chromatograms of major components (TIC) contained in sediment extract in EI mode.

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