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**Occurrence of Polybrominated Diphenyl Ethers in the Environment and
Their Biological Activity**

Bachelor thesis

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Tato bakalářská práce shrnuje poznatky o výskytu polybromovaných difenyl eterů (PBDE) v životním prostředí a domácnostech. Dále se zabývá jejich škodlivými účinky na člověka a zmiňuje metody kvalitativního a kvantitativního určování PBDE v půdních vzorcích.

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List of abbreviations

CTD	Characteristic Travel Distance
ECD	Electron Capture Detector
ECNI	Electron Capture Negative Ionization
EI	Electron Impact Ionization
GC	Gas Chromatography
LOAEL	Lowest Observable Adverse Effect Level
LRAT	Long Range Atmospheric Transport
MS	Mass Spectrometry
PBDE	Polybrominated Diphenyl Ether
PCB	Polychlorinated Biphenyls
PHWE	Pressurized Hot Water Extraction
POP	Persistent Organic Pollutants
PTV	Programmed Temperature Vaporization
SFE	Supercritical Fluid Extraction

List of some common PBDEs:

BDE 17	2,2',4-Tribromodiphenyl ether
BDE 28	2,4,4'-Tribromodiphenyl ether
BDE 47	2,2',4,4'-Tetrabromodiphenyl ether
BDE 66	2,3',4,4'-Tetrabromodiphenyl ether
BDE 85	2,2',3,4,4'-Pentabromodiphenyl ether
BDE 99	2,2',4,4',5-Pentabromodiphenyl ether
BDE 100	2,2',4,4',6-Pentabromodiphenyl ether
BDE 153	2,2',4,4',5,5'-Hexabromodiphenyl ether
BDE 154	2,2',4,4',5,6'-Hexabromodiphenyl ether
BDE 183	2,2',3,4,4',5',6-Heptabromodiphenyl ether
BDE 209	Decabromodiphenyl ether

1. Introduction

In this work, the use and function of Polybrominated Diphenyl Ethers (PBDEs) as flame retardants, their occurrence and fate in the environment and household will be discussed. Their biological activity and toxicologic effects on human will be mentioned as well. Basic determination of PBDEs in the soil samples and in the household consumables will be also reviewed.

Polybrominated Diphenyl Ethers (PBDEs) have been used as flame retardants since 1970's replacing previously used Polychlorinated Biphenyls (PCBs) which proved to be harmful to the environment and human. However, the properties and effects of the PBDEs had been doubted over the last decade, nowadays they are considered as Persistent Organic Pollutants (POPs).

Depending on the degree of bromination, there hypothetically exist 209 congeners of the PBDEs. They were used and produced as the flame retardants at three degrees of bromination: Penta-BDE, Octa-BDE, and Deca-BDE. These congeners of the PBDEs were used as additives in flammable polymeric materials like plastic components of electronics or synthetic textiles and upholstery of furniture. Nowadays only Deca-BDE is exploited, nevertheless, its harmlessness is doubted and its toxicological effects are investigated on laboratory animals [1].

Being additives, the PBDEs are not covalently bonded to the polymer molecule, but they are only dissolved in the material, often added to the product after the polymerization [2]. This procedure may be beneficial for the retardant mechanism of action. To slow down or sometimes even prevent the fire, bromine radicals are liberated in form of gas that suppress the heat and flames. This process, according to European Brominated Flame Retardants Industry Panel (EBFRIP) prolongs an escape time up to 15 times [3] in the event of fire. On the other hand, a big disadvantage of the method of additives is a gradual loss of the flame retardation property due to volatility of the PBDE additives, especially in the case of low brominated PBDEs.

Table 1 Vapor pressure, solubility and lipophilicity and solubility value for PBDE congeners, where Log K_{ow} is the octanol-water partition coefficient. Data taken from ATSDR (2004) [4].

Congener	Vapor pressure (mm Hg)	Water solubility(µg/l)	Log K _{ow}
BDE 28	1,64x10 ⁻⁵	70	5.94
BDE 47	1,40x10 ⁻⁶	15	6.81
BDE 66	9,15x10 ⁻⁷	18	-
BDE 85	7,40x10 ⁻⁸	6	-
BDE 99	1,32x10 ⁻⁷	9	7.32
BDE 100	2,15x10 ⁻⁷	40	7.24
BDE 153	1,57x10 ⁻⁸	1	7.9
BDE 154	2,85x10 ⁻⁸	1	7.82
BDE 183	3,51x10 ⁻⁹	2	8.27
BDE 209	3,2x10 ⁻⁸	<0,1	6.27

Another reason for the controversies caused by the PBDEs in past is their persistence in the environment. LogKOW values listed in Table 1 are substantially high indicating their high affinity towards lipids. Due to their lipophilicity they accumulate in tissues of animals and humans [5]. It is assumed that their toxicity and bioaccumulation properties depend on their degree of bromination; with higher content of bromine, toxicity decreases. Their toxicity [6] and effects on endocrine system [7] were also investigated with positive results.

2. Situation in the Czech Republic

The Czech Republic as a member of the European Union since 2004, maintains the status quo about the PBDEs which is the same for all members of the European Union. In 2004 the EU banned all PBDEs (except BDE 209) from their use in electronic equipments [6].

2.1. PBDEs in human breast milk

Several studies to monitor the contamination of the environment were conducted in the Czech Republic. Kazda et al. (2004) [8] investigated levels of the PBDEs in human breast milk. They analysed 103 breast milk samples and the most abundant congener was tetra-BDE 47 with a concentration of 0,86 ng/g lipid. This result was expected as the BDE 47 was the main congener used for flame retardation till 2004. Other highly concentrated congeners in the milk samples were penta-BDE 99 and hepta-BDE 183 both having concentrations of 0,28 ng/g lipid. Kazda et al. state that there is no relationship between the concentration of the PBDEs and the content of lipid in the samples or the age of mothers. They speculate that in contrast to other halogenated persistent compounds, the exposure via diet is not the most significant cause of the presence of the PBDEs in the milk samples. Skin or the respiratory system, however, may be the main routes for the PBDEs to the human body. In conclusion they mentioned that the levels of the PBDEs of the milk samples from the Czech Republic correspond to the samples from Japan or Finland.

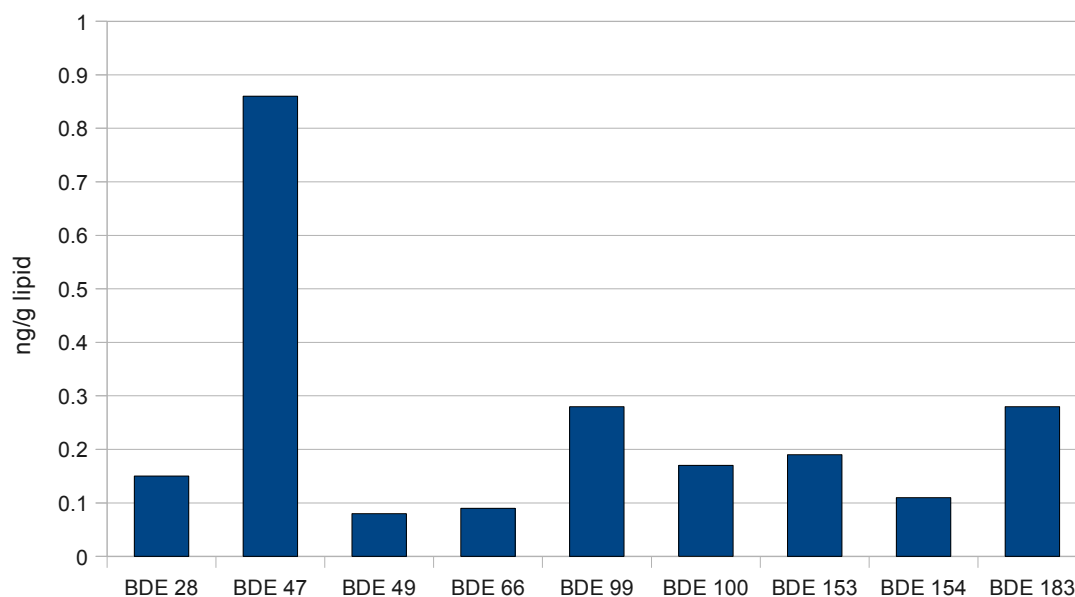


Figure 1. Concentrations of different PBDEs in human breast milk samples. Data from Kazda et al. (2004).

2.2. PBDEs in fish from the Czech rivers

Hajšlová et al. (2007) [9] monitored the extent of contamination of Czech rivers and to demonstrate the importance of fish as a transporter of energy and also contaminants to higher trophic levels, they investigated 80 fish samples. They collected three fish species with different feeding habits from eleven places on the two biggest Czech rivers Elbe and Vltava (Moldau). Again, in all three species, the most abundant congener was BDE 47. Despite different locations and different feeding habits of the examined fish, the level of all congeners was similar in all samples. The only exception was increased concentration of BDE 99 in perch. Deca-BDE 209 was not detected at all in any of the samples despite its broad use. The authors explain this absence as a result of its high excretion by aquatic species or by its instability and fast degradation during the analytical procedures.

Hajšlová et al. compared their results with previous studies from the Czech Republic in years 2001-2003, however no trends could be deduced as the levels of contamination of the rivers differ each year depending on the water flow. In years when heavy floods occur, transport of contaminated soil from areas of high pollution to areas of low pollution can be observed. When comparing the level of contamination of Czech rivers with the rest of Europe, it has to be taken into account that studies conducted for example in the Netherlands or Sweden investigated different fish species. Nevertheless the levels of contamination is comparable to Dutch and Swedish studies.

2.3. PBDEs in human adipose tissue

In 2009 Pulkrabová et al. [5] published results from their unique project of investigation the levels of the PBDEs in human adipose tissue. The adipose tissue samples were collected from people undergoing a liposuction. The operated individuals were of both genders and their age ranged from 17 to 60 years. Although the highest concentration of the PBDEs was observed in the younger patients, and the lowest concentration in older patients, no age-dependency of the concentration was confirmed.

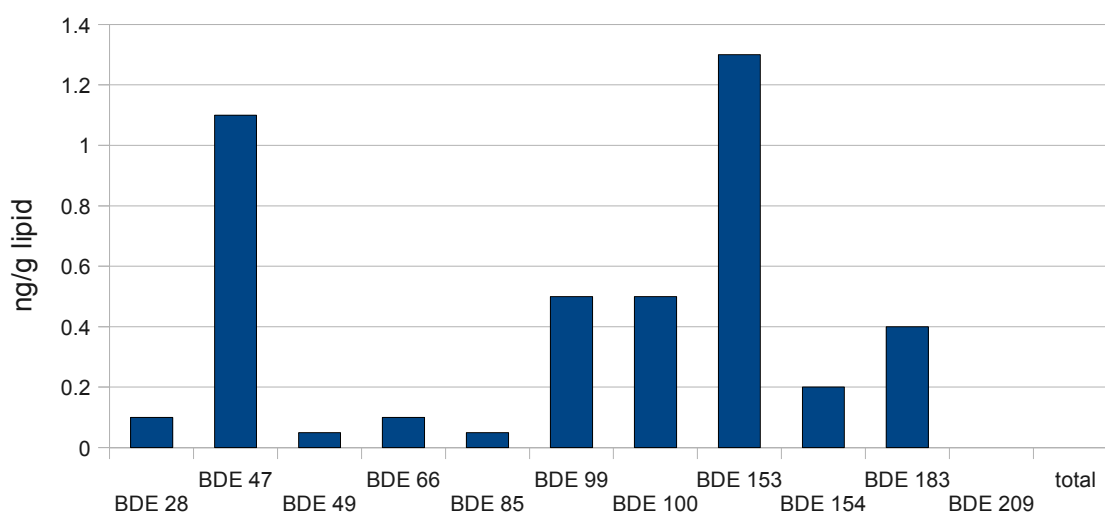


Figure 2. Concentrations of different PBDEs in human adipose tissue samples. Data from Pulkrabová et al (2009).

As Figure 2 shows, the highest levels were measured for tetra-BDE 47 and hexa-BDE 153, 1,1 ng/g lipid and 1,3 ng/g lipid respectively. BDE 153 is considered as one of the most persistent BDE, it is even more hydrophobic than BDE 47, therefore the highest level is appropriate. The congener with the lowest abundance was as usually BDE 209, probably due to its fast excretion or possible degradation.

3. Occurrence of PBDEs in the environment

3.1. Sources of pollution

The commercially produced PBDEs has been used as mixtures. The penta-BDE commercial mixtures (DE-71, Bromkal 70-5DE), octa-BDE mixtures (DE-79, Bromkal 79-8DE), and deca-BDE mixtures (Saytex 102E, Bromkal 82-0DE) [10]. BDE-47 and BDE-99 are the main components of the penta-mixtures. Even though the use of these compounds have been abolished in 2004, they are still the most abundant congeners in biological and environmental samples of various

studies [5,8,9,11]. On the contrary, nowadays the most used PBDE-209 is usually detected at low concentrations, in biological samples it is not detected at all [5,8,9]. This is explained by massive release during the recycling and incineration of old products containing penta-BDEs and minor release of the BDE-209 from the new devices [12].

In the environment the congeners with degree of bromination lower than four are typically not found [13]. Higher brominated congeners, mainly penta-BDE, octa-BDE, and deca-BDE, are found in alarming concentrations. The occurrence of these congeners is a consequence of their massive commercial production as brominated flame retardants in past (see Table 2). Prevedouros et al. (2004) [14] estimated that production of penta-BDE alone reached 5000 tonnes between the years 1970 and 2000. Another 10000 tonnes of penta-BDE were brought in finished goods in this time period.

Table 2. Production of PBDE flame retardants (metric tonnes) in 1999 and 2001. Data taken from Renner, 2000b [15] and Law, 2006 [12], respectively.

	Americas		Europe		Asia		Total	
	1999	2001	1999	2001	1999	2001	1999	2001
Deca-BDE	24300	24500	7500	7600	23000	23000	54800	55100
Octa-BDE	1365	1500	450	610	2000	1500	3825	3610
Penta-BDE	8290	7100	210	150	-	150	8500	7400

Although there exist evidences that PBDEs can be also synthesized by some biota [11,15,16] it is believed that they are not the main source responsible for such extensive pollution. The main source of pollution is considered to be the release of PBDEs from the polymer materials. Because PBDEs are not covalently bound to the polymer molecule, they can be released as vapors or in form of dust - bounded to the particle. Increased concentrations were observed during summer season when the elevated temperatures facilitate the evaporation of the PBDEs from different materials [12] to the atmosphere.

Among the major polluters are industries working with the PBDEs. The highest amounts of PBDEs are released by incineration plants. The combustion of waste that contains brominated flame retardants is the quickest and unfailing route of PBDEs to the atmosphere. Although in places of the main pollution source, the concentrations of PBDEs are perpetually high, the PBDEs can be also found in the atmosphere above rural areas and places distant from the sources of pollution [17]. After the rain, however, the levels of PBDEs in the atmosphere were lower which was explained by washing out of the compounds together with the particles to which they are bound.

3.2. PBDEs in sewage sludge, sediments and soil

PBDEs have been also found in the sewage sludge. Monitoring of the levels of PBDEs in the sewage sludge is very important as the sludges are utilized in the agriculture. Their use as fertilizers can induce a transfer of PBDEs to the crops and subsequently to the human bodies. Even though there are not many studies about the levels of PBDEs in the sewage sludge in Europe, there are some studies investigating the sewage sludge in Spain, Austria, and Denmark [18, 19, 20]. Although the concentrations varied in each country, the main congeners identified in the sludge samples were BDE 47, BDE 99, BDE 100, BDE 153, and BDE 183. BDE 209 was prevailing PBDE, exceeding the sum of all other congeners up to two times.

Sediments and soils are also rich in PBDEs pollutants. PBDEs are found in river and coastal sediments across the Europe. General tendency is that the concentration of PBDEs increase as the river flow advances the sea. This trend is explained by simple accumulation of the PBDEs along the watercourse. Contribution of individual PBDEs differ depending on the PBDE mixture commercially used in given country or the extent of urbanization and distribution of industries along the rivers. In sediments of Austrian river Danube, for example, BDE 47 and BDE 99 were the predominating congeners [21]. Samples from sediments of river Elbe, collected in the Czech Republic and Germany, contained the highest amounts of BDE 209 [22], the concentrations of other congeners depended on the local industries of the two countries.

Application of the sewage sludge to the soils to fertilize and increase crops is another source of PBDEs in the soils and surface sediments. A certain Swedish research of agricultural soils [23] reported that PBDEs can remain in the soil for more than 20 years. It is therefore inevitable that these compounds are taken up by range of organisms and due to their lipophilicity they accumulate in the bodies of animals and further expand to the higher levels of the food chain. Together with flow of the energy across the food web, the PBDEs are transferred from the lower to the higher trophic levels. As a result of this mechanism the PBDEs are bio-accumulated and bio-magnified.

3.3. PBDEs in biota

As discussed above, the PBDEs are present in the biota of the lowest trophic level, for example earthworm, fresh water and marine fish and invertebrates and even in zooplankton [24]. Going up the food web, PBDEs are also found in birds and their eggs. A study of the North Sea [25] illustrate the extent of the biomagnification. Boon et al. (2002) analyzed the amounts of PBDEs in several species of the North Sea. The results showed that the lowest concentration were in invertebrates, up to three times more PBDEs were detected in fish, and nine times more in harbor

seal blubber, which is on the top of the food chain. The main congener detected in biota was BDE 47, BDE 209, on the other hand was not detected at all or in very low concentrations (see Table 3). The most alarming fact about the extent of pollution of the environment is the presence of PBDEs in the marine mammals, such as baleen whales and beluga whales which are found in places of the oceans remote from the civilization.

Table 3. Mean concentrations of some PBDEs in marine and freshwater organisms ($\mu\text{g}/\text{kg}$ wet weight). Data taken from Hajšlová et al. (2007) [9] and Law et al. (2006) [24].

Sample	Location	BDE 47	BDE 99	BDE 100	BDE 153	BDE 154	BDE 209	Σ BDE
perch	Czech republic	2,5	0,2	0,5	0,1	0,2	n.d.	3,9
zooplankton	Canada	0,66	0,46	0,13	n.a.	n.a.	n.a.	1,5
shrimp	Canada	0,17	0,02	0,03	n.a.	n.a.	n.a.	0,24
beluga whale	Canada	258	100	59	n.a.	n.a.	n.a.	493
dolphin	England	121	99	38	25	n.a.	n.a.	353
fin whale	England	13	12	5	n.d.	n.a.	n.a.	38

n.a. - not available

4. Fate of PBDEs in the environment

4.1. Long-range atmospheric transport

In 2003, Gouin and Harner [26] tried to model the fate of PBDEs in the environment. They tried to explain why the PBDEs appear also in places remote from the sources. The calculated potential for long-range atmospheric transport (LRAT) for five PBDEs with different degree of bromination (from 2 to 6). They considered degradation of these congeners in soil and water by microbes, and degradation in the atmosphere by reaction with hydroxyl radicals. Taking into account also vapor pressure, solubility in water, octanol-water and octanol-air partition coefficient they calculated characteristic travel distance (CTD) for each of the investigated congener.

From the specific CTDs they deduced that PBDEs with four or less bromine atoms are capable of LRAT. On the contrary, higher brominated molecules lack the ability of LRAT which is eventually inconsistent with the empirical values. The fact that heavier congeners are found in remote locations as well was explained by their novel hypothesis. The heavy PBDE congeners released from the source travel their CTD which is rather short compared to the light congeners. When winter comes, they are washed out from the atmosphere and trapped in the snow cover. When melting occurs, they re-evaporate, they cover the CTD again. The cycle repeats every year and in this fashion, the heavy congeners are transported even to the very distant places.

4.2. Degradation of PBDEs

Schenker et al. [27] were more interested in the degradation of the highly brominated congeners, mainly deca-BDE. They decided to neglect microbial degradation and degradation by hydroxyl radicals and supposed that the direct photolysis is the chief mechanism proceeding with PBDEs in both gaseous and aerosol forms. They calculated that the elimination occurs step-wise with one bromine atom eliminated in each step. Each elimination degree in deca- to hexa-debromination yields up to 80% whereas additional debromination yields less than 50%.

The authors contradict the theories that explained elevated concentrations of BDE 209 in soil and decreased concentrations in the atmosphere by effective scavenging by rainfalls and its consequent deposition in the soils and sediments. They claim that the decreased concentrations of deca-BDE to hepta-BDE in the atmosphere are in 45% due to the photolytic degradation and in 30% due to the deposition into the soil. They further state that 50% of the concentration of hepta-BDE and hexa-BDE are the products of the debromination of BDE 209. Photolytic debromination reaction is also the source of 3-20% of penta-BDE in the atmosphere. In conclusion, Schenker et al. suggest that the products of the debromination of BDE 209 can slow down the decrease of penta- and tetra-BDE from the atmosphere after their ban in EU.

5. Occurrence of PBDE in the household

Although penta- and octa-BDE mixtures are no more used, they may still be present in households in old consumer devices. The penta-BDE formulation was used in polyurethane foams which are essential parts of the mattresses, cushioning in various upholstered furniture. The octa-BDE mixture was predominantly used in business offices in high-impact ABS (acrylonitrile-butadiene-styrene) plastic in computers, telephones, and other machines necessary in the office. The octa-formulation was also used in automobile boards. The deca-BDE has been used to decrease risk of fire in carpets, high-impact polystyrene of various electronic devices (TV sets, computers, stereos etc.) or cable insulation [6].

It is clear that PBDEs have been widely used in range of equipment of the household. Even though there have been number of studies analyzing the atmospheric concentrations of the PBDEs. Rudel and Perovich (2009) think that the measurements of indoor concentrations are more important to understand the extend of the human exposure as people stay vast majority of their time indoors [28].

The PBDEs are released continuously from the polymer materials, in case of higher temperatures (especially in summer season) the rate of release is even faster. The congeners with higher degree of bromination tend to bind to the dust particles. Jones-Otazo et al. [29] believe that

dust particles containing the PBDEs is the main path of exposure to the human, especially to infants and toddlers. Taking into account several designs, they came up with a theoretical intake value of 155ng/day for adults and 1965ng/day for breast-fed infants which corresponds to 2 and 280 ng/kg body weight respectively. They claim that over 60% of total exposure in average adult individual is due to ingestion and inhalation of dust the contaminated particles. In children of age between 0,5 – 4 year the ingestion of the dust can reach even 90% of total daily intake of PBDEs. In response, environmental organizations advice several methods and precautions to decrease the risk of exposure to PBDEs [30].

6. Biological activity

Besides the direct exposure during the production or destruction of the products containing the brominated flame retards, there are several ways of exposures to PBDEs. One of the pathways is ingestion of the contaminated food (e.g. fish, or milk products), other way is inhalation and ingestion of the vapors or the dust particles, or even skin contact [11, 29]. The PBDEs can reach also fetus through placenta, or infants via breast milk.

6.1. Endocrine disruption

PBDEs are suspected to belong among endocrine disrupting chemicals, therefore their exposure to the fetuses and infants may be of enormous danger. PBDEs are structurally similar to thyroid hormones T3 and T4 (thyroxine). Hydroxylated PBDE metabolites [7] eagerly bind to thyroid hormone receptors so that the production of the thyroid hormone cease which is followed by decrease of level of these hormones in blood serum. Endocrine system is very sensitive and any interference induce disruption of the system [11].

The disruption may have serious impact especially on fetal development. Exposure during the gestation period or during the first three years of life may lead to damage of brain development. Several studies on mice and rats have been proceeded, for example Eriksson et al. (1999) [31] observed that BDE 47 applied few days after birth caused problems in learning and memory in mice. The problems were increasing with age of the mice. Mice exposed to BDE 209 proved to have these problems [2].

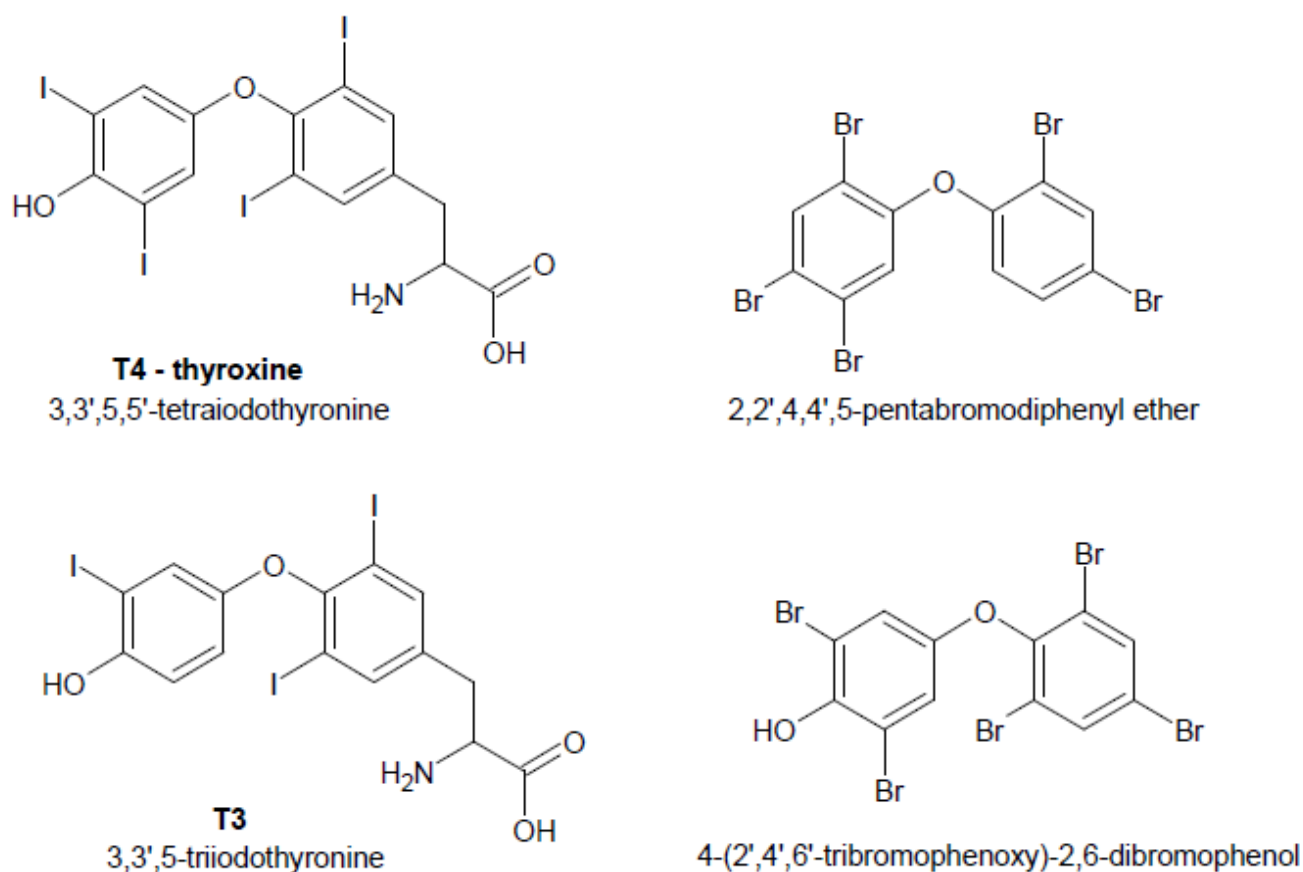


Figure 3. Structural formulas of thyroid hormones and structurally similar penta-PBDE and its hydroxylated metabolite.

6.2. Neurotoxicity and carcinogenicity

McDonald (2002) [7] suggests that the brain development disturbance is caused by the disruption of the thyroid hormone. This hormone is vital for brain development in fetus and also newborns by controlling several processes such as proliferation of neural and glial cells, myelination or neural migration and differentiation. Another factor influencing the proper brain development is the interference with the second messenger pathways. This kind of interference can for example cause an imbalance of calcium ions which are responsible for correct function and development of neuron cells.

Although several tests on the toxicity of PBDEs on mice and rats resulted in number of adverse effects on brain development it is not very clear how far are these observations applicable to humans. Doses administered to the experimental animals were often many times higher than levels measured in human tissue. Scientists are convinced that potential risk is in pregnant women, fetuses and children. Members of this group are susceptible towards thyroid hormone disruption. The extend of exposure to PBDEs in fetuses and infants is greater than in developed man. In pregnant women the need for thyroxine hormone to maintain the homeostasis is considerably

higher, even though there is remarkable shortage of iodine due to increased function of the kidneys [7]. Not to mention that there is an increasing number of iodine deficient people. Nevertheless, addition of iodide into the diet during the gestation period remarkably decrease the risks that are connected with thyroid hormone disruption.

When comparing the neurotoxicologic effects of individual commercially used congeners, the most harmful appeared to be penta-BDE with the LOAEL (Lowest Observable Adverse Effect Level) of 0,6-0,8 mg/kg body weight [32]. The LOAEL for the octa-BDE was estimated to 2 mg/kg body weight. The highest LOAEL assessed to 80 mg/kg body weight for deca-BDE.

Carcinogenic study on deca-BDE showed that deca-BDE can cause tumor at doses of 1200 mg/kg body weight per day [32]. This portion of deca-BDE is very high even when compared to people with daily exposure to the BDE 209 due to their profession. Furthermore, the deca-BDE is poorly absorbed (about 1%) when ingested and very quickly excreted in faces [6]. Carcinogenic effects of other congeners have not been proved so far.

7. Basic determination of PBDE in the soil samples

7.1. Sample preparation

Sediment and soil samples are very heterogeneous, therefore they require thorough pretreatment. The sample is advised to be dried to avoid tiring liquid-liquid extractions in further sample handling. Water evaporation and subsequent treatment with anhydrous sodium sulphate seem to be optimal method [33]. Because the soil samples usually contain quite a big amount of sulfur, it has to be eliminated by mixing the homogenized sample with copper powder [34].

7.2. Extraction

The sample pretreatment is usually followed by a solid-liquid extraction with acetone and acetone/hexane used as solvents [34]. Simple solid-liquid extraction may not be sufficient for the extraction of PBDEs from the soil matrix. Soxhlet extraction with hexane, toluene or dichlormethane as solvents is convenient alternative. Soxhlet extraction at elevated temperature even decrease the extraction time to 6 hours [33]. Special care has to be taken about BDE-209. It is recommended to eliminate UV-radiation in the laboratory, because BDE-209 is known to be labile under the UV-light. Also dust should be removed for example by ionizers, to decrease the loss of BDE-209 due to its binding to the dust particles.

Supercritical fluid extraction with solid phase trapping (SFE) with CO₂ as the

supercritical fluid or an extraction with pressurized hot water (PHWE) offers faster extraction. The extracts from SFE and PHWE are very clean compared to the extract of the Soxhlet extraction so that further cleanups before GC analysis can be skipped. These two methods significantly reduced time demanded for the extraction. The time shortage and cleanliness of the extract considerably and deplete the chance of making and accumulating errors influencing the analysis.

Another effective method is the solid-liquid extraction with the help of ultrasonic waves. Sanchez-Brunete et al. (2006) [35] extracted the PBDEs from the soil sample in a glass columns dipped into ultrasonic bath. For the extraction they used 2x 5 ml of ethyl acetate, the extraction time 2x 15 minutes. This method is advantageous due to use of small amount of the extraction solvent and due to its minimal time demand. Another advantage is that no special pretreatments have to be taken to remove soil moisture from the sample.

As was mentioned above, the product of the solid-liquid or the Soxhlet extraction may not be of high purity and further clean-up is usually necessary. It is recommended to clean the crude extract by an alumina column. As an elution solvent hexane in combination with iso-octane is used [34]. For deca-BDE dichloromethane or mixture of acetone and hexane is preferred, since the BDE 209 is not soluble in iso-octane [33].

7.3 GC analysis

PBDEs are frequently separated by Gas Chromatography (GC). However several factors can alter the analysis and results. The choice of each component of the GC instrumentation and appropriate programming of the instrument is crucial for precise analysis and reproducible results. Correct sample preparation together with suitable GC instrumentation can prevent the loss and degradation of highly brominated PBDEs, especially nona-BDEs and deca-BDE which are easily degraded to lower brominated congeners, resulting in distortion in the results of the analysis.

The type of injector and selection of proper injection mode is crucial for the PBDEs analysis. The most commonly used injectors are splitless and on-column injector. While the on-column injector is appropriate for clean sample such as atmospheric samples, for more complex samples, such as soil and sediment, the Programmed Temperature Vaporization (PTV) injector is suitable [36]. Björkulund et al. (2004) [36] found out that application of temperature gradient and pulsed pressure is the optimal mode for quantitative analysis of all PBDEs including BDE 209.

The use of proper capillary columns can also significantly alter the analysis of PBDEs. The best columns seem to be 5% phenyl-methylpolysiloxane column [36]. Almost non polar 5% phenyl-methylpolysiloxane column showed almost no degradation of BDE 209 compared to the losses of amounts in BDE 209 in 35% phenyl-methylpolysiloxane column of midpolarity. Not only

the polarity of the GC column influences the yields of PBDEs but also the length of the column is to be chosen carefully. It has been observed that the longer the column is, the longer time the PBDE molecules spend in it having a negative impact on their degradation.

Last, but not least parameter for the successful quantitative and also qualitative determination of the PBDEs in the temperature of the column during the analysis. Too low temperature results in band broadening which can counteract the separation aimed in the GC column. High temperature, in contrast, give rise to the degradation of nona- and deca-BDEs. A GC oven adjusted to a temperature of 300°C is believed to be most favorable.

7.4 Detection

For detection of PBDEs after the GC column, mass spectrometry (MS) or electron capture detection (ECD) has been widely used. Due to decreased sensitivity of the ECD especially to tetra- and higher congeners, the MS detection is preferably used. Mostly used mass spectrometers use electron impact ionization (EI) detector or electron capture negative ionization (ECNI) detection mode. Although the ECNI detection requires high purity of the sample it is commonly used especially when analyzing samples with very low content of PBDEs. The EI detector, despite bit lower sensitivity, can simultaneously detect other compounds present in the sample [33]. The optimal conditions for precise analysis of the PBDEs in sediment and soil samples which compromise both accuracy and cost are listed in Table 4. Example of GC-ECD spectrum with the is depicted in Figure 4.

Table 4. Optimal conditions for PBDEs analysis in sediment and soil samples.

sample pretreatment	homogenization with copper powder
extraction	Solid-liquid with ultrasonication
GC injection	PTV
column	5% phenylmethylpolysiloxane, 15 m length
oven temperature	300 °C
detection	MS-ECNI

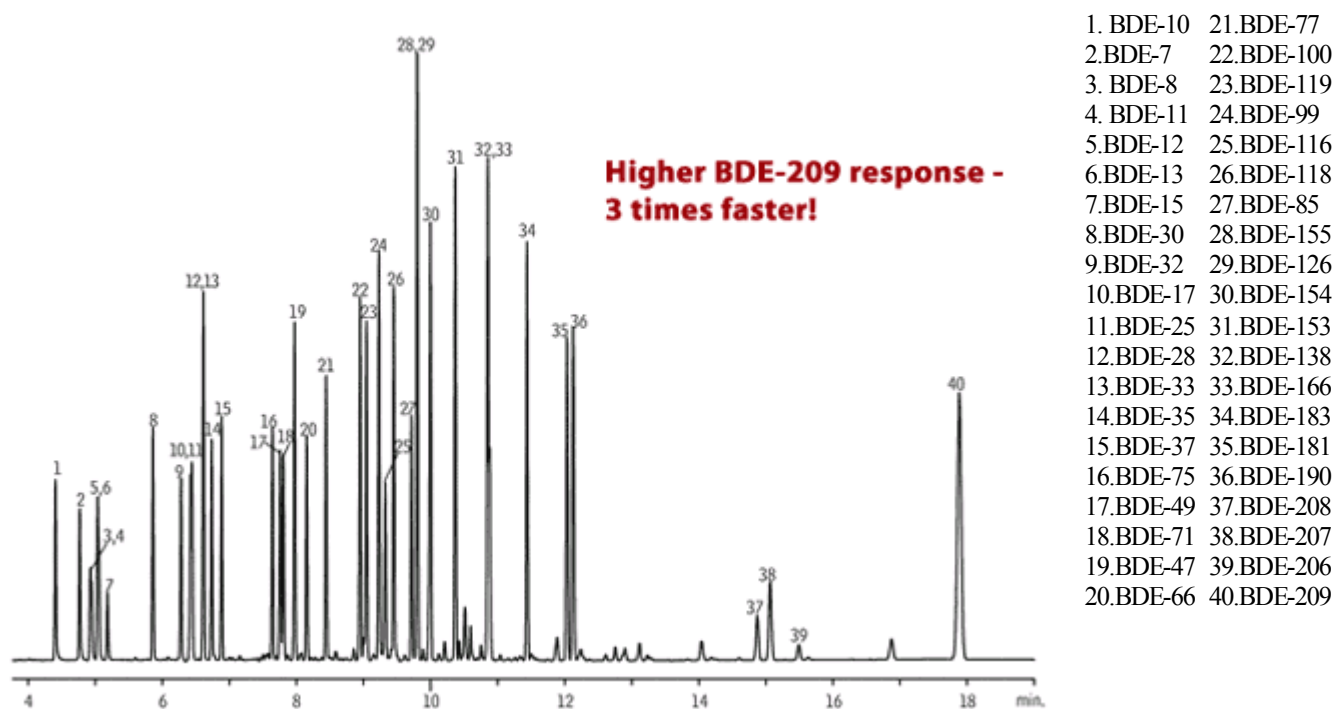


Figure 4. GC-ECD spectrum of PBDEs using Rtx®-1614 column (5% phenylmethylpolysiloxane, 15 m length), splitless injection, oven temperature 300°C, ECD detection mode. Picture adopted from [37].

8. Conclusion

Polybrominated diphenyl ethers are spread all over the world; in the atmosphere, soil, deep oceans, biota, and also human. Although their concentrations in the environment should not increase significantly due to their ban in Europe, USA and Canada, it has been proved that they are persistent in the environment. Several studies investigated the extent of pollution, bio-accumulation and toxicological effects. Not many researches devoted their work to the reduction of the environmental concentration of PBDEs. Degradation of PBDEs by bacteria or different methods of decomposition should be developed to diminish the amount of PBDEs in the environment.

Abstract

Polybrominated Diphenyl Ethers (PBDEs) had been used as additives into several polymer materials as flame retardants since 1970's. They are released from the polymer material to the atmosphere and transferred to remote areas. PBDEs can be also found in sediments and soils, therefore they are taken up by organisms. Due to their lipophilicity they are accumulated in the animal bodies and they are transferred to higher trophic levels.

Humans are exposed to the PBDEs by consumption of contaminated fish or by inhalation and ingestion of vapors and dust particles containing the PBDEs. PBDEs can also reach the fetus through placenta, or infants via breast milk. Due to their structural similarity to thyroid hormones, they easily bind to thyroid hormone receptor causing a disruption of the thyroid hormone homeostasis. The disruption may have serious impacts especially on fetal development.

The PBDEs can be extracted from the soil sample by means of Soxhlet extraction, SFE, or by solid-liquid extraction with the help of ultrasonication. The extract is then analyzed by GC with PTV injection, 5% phenyl-methylpolysiloxane column and 300°C oven temperature. The detection of the PBDEs is done by ECNI-MS or by EI-MS.

Souhrn

Polybromované difenyl etery (PBDE) byly používány od 70. let 20. století jako aditiva do různých polymerů jako látky zpomalující hoření. Tyto látky se z polymerů uvolňují do atmosféry a jsou transportovány do vzdálených oblastí. PBDE se nacházejí také v sedimentech a půdách, takže jsou vstřebávány různými organizmy. Kvůli jejich lipofilitě jsou PBDE akumulovány v tělech živočichů a jsou dále přenášeny do vyšších trofických stupňů.

Lidé jsou vystavováni PBDE konzumací kontaminovaných ryb nebo vdechováním par a prachových částic obsahujících PBDE. PBDE se také mohou dostat do plodu přes placentu, a kojenci mohou být exponováni pitím mateřského mléka. Vzhledem k podobnosti jejich struktury ke struktuře hormonů štítné žlázy, se lehce váží na receptory hormonu štítné žlázy a tím narušují homeostázu těchto hormonů. Toto narušení může mít vážné důsledky obzvláště na vývoj plodu.

PBDE jsou extrahovány z půdních vzorků Soxhletovou extrakcí, SFE nebo extrakcí kapalina-pevná látka s pomocí ultrazvuku. Extrakt je posléze analyzován GC s PTV vstříkem, 5% fenyl-metylpolysiloxanovou kolonou a teplotou termostatu 300°C. PBDE jsou detekovány pomocí ECNI-MS nebo EI-MS.

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