FIRST ATTEMPT TO MEASURE PBDE LOADS IN LEACHATES FROM LANDFILLS IN POLAND

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Abstract
Brominated Flame Retardants (BFRs) are a group of chemicals which are produced with the purpose of protecting human life, health and property from fire. As a consequence of the chemical stability of these compounds, the brominated flame retardants have a tendency to accumulate and spread in the environment also in landfill leachates which can be a potential source of them on the way solid wasters – lechates – surface waters.
There was no production of BFRs in Poland in the past and there is not presently, but a lot of products containing BFR are available on the market. First attempt to measure PBDE levels in leachates from landfill of municipal wastes in south eastern Poland was made. For analysis of selected PBDE extraction on SDB-XC (3M) discs was applied. Additional clean-up on *Envirogel* columns and final analysis of extracts with GC-MS *Trace Ultra-Polaris Q* system.
Six landfills of different capacity and history were selected. Measured concentrations varied in the respect of particular PBDE and particular landfill. The highest concentration of 2,2',4,4',6 -PeBDE (PBDE-99) was obtained in samples taken from the biggest landfill. Concentration of other PBDE were significantly lower. Concentrations in the leachates from small landfills collecting wastes from rural area were below detection limits for most of the examined substances.

Introduction

Brominated Flame Retardants (BFRs) are a group of chemicals which are produced with the purpose of protecting human life, health and property from fire. They have some technical advantages in many types products, made from flammable materials (plastics, textiles, furnishing foam, paints, rubber). BFRs are commonly used in domestic and industrial appliances and equipment, e.g. computers, printers, TV sets, mobile phones, mattresses, insulation boards. During the last decades, the consumption of brominated flame retardants has globally grown due to the growth in the use of flammable synthetic polymers in consumer products (which have replaced less – combustible natural materials), and the introduction of more rigorous fire safety requirements. Moreover, using of BFRs are the cheapest way of improving fire resistance compare to others flame retardants available on market.
In spite of the uniform mechanism of action, BFRs are highly differentiated group of compounds – aliphatic and aromatic, reactive and additive. Aliphatic appear to have less thermal stability than the aromatic ones. Hence, aromatic are used extensively as flame retardants all over the world. In a case of reactive flame retardants, they are incorporated into the polymer materials by a covalent bonding between the polymer and the flame retardant, whereas the additive types are dissolved in the polymer[1]. Additive flame retardants are sometimes volatile and that is why they can tend to leach out, and enter the environment more easily.
The most commonly used BFRs are polybrominated diphenyl ethers (PBDEs), tetrabromobisphenol A (TBBPA) and hexabrominated biphenyl (Fire Master BP-6). Most industrially manufactured PBDEs are mixture of brominated diphenyl ethers, their isomers and homologues. Commonly used are Penta-BDE, Octa-BDE and Deca-BDE.
As a consequence of the chemical stability of these compounds, the brominated flame retardants have a tendency to accumulate and spread in the environment. This accumulation in combination with some environmental adverse effects of the compounds has during the last decade placed the brominated flame retardants in the international attention. Many of these chemicals are suspected endocrine disruptors and as well as bioaccumulative and persistent in the environment[2]. During the last few years new results showing that brominated flame retardants are emitted from products in use and are present in the human body and breast milk in measurable quantities have further increased the focus on the compounds.

The problem of bromoorganic compounds in Poland have not been studied until very recently. There is no information about levels of these compounds in the environmental compartments. There was no production of BFRs in Poland in the past and there is not presently, so no point sources have been located. However, in the Polish environment brominated flame retardants and their byproducts, can be entered by long-range transport and by emission and releases due to washing out, evaporation and incineration of products such as textiles, TV sets, computer equipment and from polyurethane foam applications. Last years Poland became a country where a lot of international companies produce LCD monitors and TVs. Higher living standard in Poland over recent years resulted in replacing old electronic equipment by new items in many households. Legal regulations concerning separate collections of electronic wastes from households were introduced year ago.

Two sources of PBDE connected with waste utilization should be under special control in Poland, as potentially the most hazardous ones: uncontrolled waste incineration in households, where plastic appliances might be combusted in low temperature, and waste landfilling, which is still the most popular way of waste processing in Poland.

In most of the cases, landfill leachates are treated together with municipal sewage in the municipal wastewater treatment plant, so persistent pollutants are cumulated in the sludge and might be introduced again into the environment if sludge is utilized in agriculture. Leachates are important source of PBDEs via solid waste – leachates – surface water/or sludge pathway.

Materials and Methods

Six landfills in south eastern Poland were selected for experiment, including the biggest landfill in the region (site 1). This site was established as a municipal landfill for the 400 thousand Lublin community in 1994. For seven years municipal wastes were deposited at landfill without any segregation. Sites 2 and 3 were also considerably big and collecting waste from municipal area. The other landfills – site 4, 5 and 6 were located near small towns, therefore wastes deposited on them were typical rather to rural area (less plastics, more ashes). Sites 4, 5 and 6 were also smaller in the respect of amount of wastes deposited.

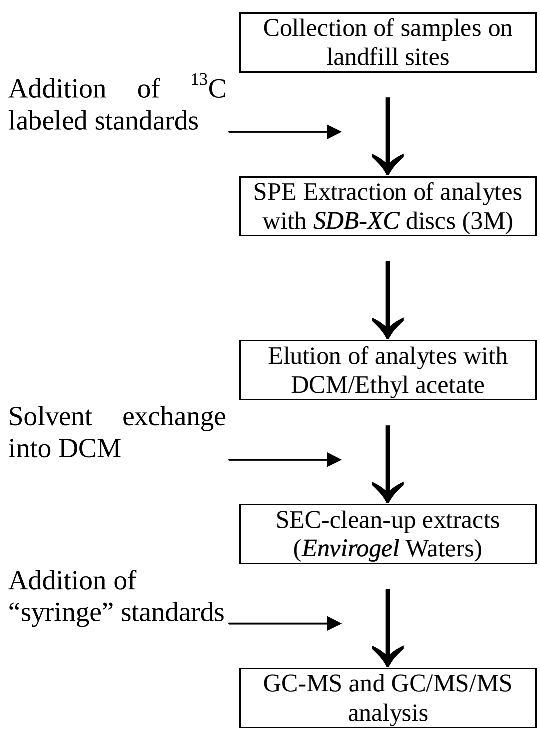

Figure 1. Scheme of steps in the analysis of leachate samples for PBDE.

Leachates were collected to dark glass containers, transported to the laboratory and analyses immediately. The analytes from samples were extracted with fully glass SPE system with SDB-XC discs (3M, USA) previously conditioned with dichloromethane, methanol, 2-propanol (all solvents for residue analysis grade, JT Baker, Germany). Extraction of analytes were done with a mixture of dichloromethane and ethyl acetate. The extract was evaporated under a nitrogen stream and after solvent exchange into dichloromethane purified using size exclusion chromatography (SEC) on Brezee 1525 (Waters) system equipped with *Envirogel* columns. Analytical procedure is presented in Figure 1.

Final analysis was done on the *Trace Ultra – Polaris Q* GC-MS system. Parameters of the system are presented in Table 1. Applied method allowed to determine PBDE containing from 4 to 6 bromine atoms, therefore only 2,2',4,4'-TeBDE (PBDE-47), 2,2',4,4',6-PeBDE (PBDE-99), 2,2',4,4',5-PeBDE (PBDE-100), 2,2',4,4',5,5'-HxBDE (PBDE-153), 2,2', 3,4,4',5'-HxBDE (PBDE-138) were measured. Detection limit for this method was evaluated on 0.5 ng/dm^3 (S/N=3), quantiation limit was evaluated on the level 1 ng/dm^3 (S/N=5).

Table 1. Conditions of GC-MS system.

The operation conditions of the chromatograph (TRACE ULTRA):	
Injector:	PTV (splitless mode) @ 320^{o}C
Capillary column:	RTx Dioxin (Restek) 60m x 0.25mm d_f=0.18µm
Oven temperature programming:	85^{o}C (0.5 min hold) ramp 15^o/min to 210^{o}C then ramp 5^o/min to 320^{o}C, 5 min hold
Carrier gas:	He (99,9996%) @ 40 cm/s
The MS operating conditions (POLARIS Q):	
The ion source temperature	250^{o}C
The transfer line temperature	275^{o}C
Scanning mode I: ***Full Scan***	50.0 - 850.0 amu
Collision gas	He (99,9996%) @ 2 ml/min
Scanning mode II:	SIM: quantitation ion and (qualifiers) Te-BDE 486 (326) Pe-BDE 564 (566, 406) Hx-BDE 644 (484, 482)

Results and Discussion

Obtained results are gathered in Table 2.

As it might be seen , concentrations varied in the respect of particular PBDE and particular landfill. The highest concentrations were found for 2,2',4,4',6-PeBDE (PBDE-100) and 2,2'4,4'-TeBDE. Concentration of hexa-substituted compounds were lower. The highest concentrations were observed for the biggest landfill (Site 1), despite 2,2',4,4',5,5'-HxBDE, with concentration was below detection limit. Site 1 is landfill which collecting wastes from the city of Lublin (350, 000 inhabitants).

Table 2
Results determination of PBDE in leachate samples from different landfill sites [ng/dm^3].

PBDE	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6
2,2’,4,4’-TeBDE	214	51	73	ND	8	12
2,2’,4,4’,6-PeBDE	232	121	61	ND	33	23
2,2’,4,4’,5-PeBDE	73	ND	9	ND	ND	ND
2,2’,4,4’,5,5'-HxBDE	ND	44	26	ND	ND	ND
,2', 3,4,4',5'-HxBDE	31	24	ND	ND	ND	ND

Lower concentration were observed for small landfills collecting wastes from less developed rural area, although only for Site 4 all examined compounds were below detection limit. For other landfills, concentrations of 2,2’,4,4’,6-PeBDE (PBDE-100) and 2,2’4,4’-TeBDE were measurable, and concentrations of 2,2’,4,4’,6 –PeBDE were slightly higher. Concentrations of PBDE in the leachates from small landfills were comparable to the highest concentrations found in the Vistula River (unpublished own data).

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References
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