Polybrominated Diphenyl Ether Levels in Livers of Predatory Birds from Poland

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Introduction.

Polybrominated diphenyl ethers (PBDEs), a class of polyhalogenated organic compounds have became recently an important group of environmental pollutants. Their ubiquity in the environment refers to their wide use as an additive flame retardants in a variety of plastic consumer products (Alaee et al. 2003; de Witt 2002). PBDEs have emerged as a subject of great concern, because of their increasing levels in biological samples, including humans, animals, especially birds, fish and marine mammals. Additionally, there are strong evidences suggesting high ability of some PBDE congeners to bioaccumulation and biomagnification in a food chain. Several studies indicate that PBDEs can cause disturbance of the thyroid hormone homeostasis and chronic neurotoxicity (McDonald 2002). It is a well-known, that birds of prey, occupying top position within thropic web can accumulate pollutants in their tissues, for example toxic metals or persistent organic pollutants (POPs), especially organohalogenated chemicals like pesticides, PCBs, dioxins (Wienburg et al. 2004). Moreover, different bird of prey species belong do the different ecosystems (terrestrial or aquatic) and have different food preferences (small terrestrial animals, insects, eggs, carrion, wastes from landfills) and habits (diurnal or nocturnal). Hence, they have been widely used as very sensitive biomonitors of the environment contamination with different kinds of chemicals (Jaspers et al. 2006; Naert et al. 2007). In connection with such statement, many studies have been conducted on predatory birds focusing on their eggs (Herzke et al. 2002, 2005), feathers (Jaspers et al. 2007), muscles, blood and livers (Law et al. 2002; Voorspoels et al. 2006). The use of liver as a method for the evaluation of POP concentrations is known because of high content of lipid it has, and the role this organ plays in metabolism of toxic chemicals.

In this study we report levels of selected PBDE congeners (BDE 28, 47, 52, 77, 99, 100, 138, 153, 180, 183) in liver of terrestrial predatory birds *Falconiformes* mean by diurnal: common buzzard (*Buteo buteo*), kestrel (*Falco tinnunculus*), goshawk (*Accipiter gentelis*), marsh harrier (*Circus aeruginosus*) and nocturnal barn owl (*Tyto alba*). This is the first, pilot study conducted in order to obtain preliminary data about the concentrations of PBDEs in Polish predatory birds.

Materials and Methods.

Sample collection

Birds were collected from 2007 to 2008 at different places in Poland (Table 1). All birds were found death or had died shortly after collection. The predominant causes of death were traffic accidents, electrical shock, shooting, natural causes or starvation. No birds were killed for this study.
Samples preparation and chemical analysis of target PBDEs were done in the Laboratory of Environmental Analysis, Lublin University of Technology, Faculty of Environmental Engineering,

Poland. Excised livers were wrapped in aluminium foil in order to avoid any contact with external surface and stored at -20^{0}C until further treatment.

Table 1. Location and characteristics of the sampling birds.

Terrestrial predatory bird species						
English name	**barn owl**	**common buzzard**		**kestrel**	**marsh harrier**	**goshawk**
Latin name	*Tyto alba*	*Buteo buteo*		*Falco tinnunculus*	*Circus aeruginosus*	*Accipiter gentelis*
Sampling place	Tarnowskie Góry	Warszawa	Mikołów	Warszawa	Mikołów	Biała
Year	2007	2007	2007	2008	2008	2008
Lipid (%)	8.1	4.9	6.4	7.2	5.6	6.2

Chemicals

All chemicals used for PBDE analysis were of high purity. Toluene and dichloromethane (Ultra-Resi Analysed) were purchased from T.J. Baker (Germany). PBDE analytical mixture standards series BDE-CVS-F containing BDE 28, 47, 52, 85, 99, 100, 153, 154, 183 congeners, as well as mass labeled (^{13}C) PBDE recovery solution BDE-MFX containing BDE 77L and 138L were obtained from Wellington Laboratories (Ontario, Canada). Additional standard solutions of native PBDE containing BDE 28, 47, 85, 99, 100, 153, 183 congeners were obtained from Wellington Laboratories and from AccuStandards (mixture M-527 BDE).

Analysis of PBDEs

Approximately 3-5 g of liver was homogenized and then dried by blending with anhydrous sodium sulfate in a mortar. Subsequently, samples was extracted with toluene in a Soxhlet apparatus for 8 hours in a dark room. Extracts were concentrated using a rotary evaporator, and lipid content was determined from an aliquot of the extract gravimetrically. Further purification was performed using size exclusion chromatography (SEC) (Brezee 1525, Waters). The analysis of target BDE congeners was done using the Trace Ultra – Polaris Q GC-MS system. Analytes were separated on a 60 m RT_x Dioxin capillary column (Restek, 0.25mm i.d., 0.18 μm film thickness) operating with helium carrier gas (constant velocity 40 cm s^{-1}) under the following temperature program: from 85°C (0.5 min hold) ramp 15° min^{-1} to 210°C, then ramp 5° min^{-1} to 320°C, 20 min hold. The temperature of injector was set at 320°C. The temperature of the transfer line, and ion source was 275°C, and 250°C, respectively. The identification of the total of 10 PBDE congeners in the liver samples was based on their MS data and retention times with those of reference standards and those reported in the literature.

Results and Discussion.

In general, all target PBDE congeners were found in all liver samples. The maximum concentrations of selected congeners (reported in ng g^{-1} on the lipid contents) were as followed: BDE 28 – 203.1, BDE 47 - 1359.3, BDE 52 - 296.9, BDE 77 - 464.3, BDE 99 - 666.7, BDE 100 - 171.9, BDE 138 - 609.4, BDE 153 - 1035.7, BDE 180 - 665.5, and BDE 183 – 89.3.

The percentage distribution of the measured PBDE congeners in bird livers is plotted in the Figure 1.

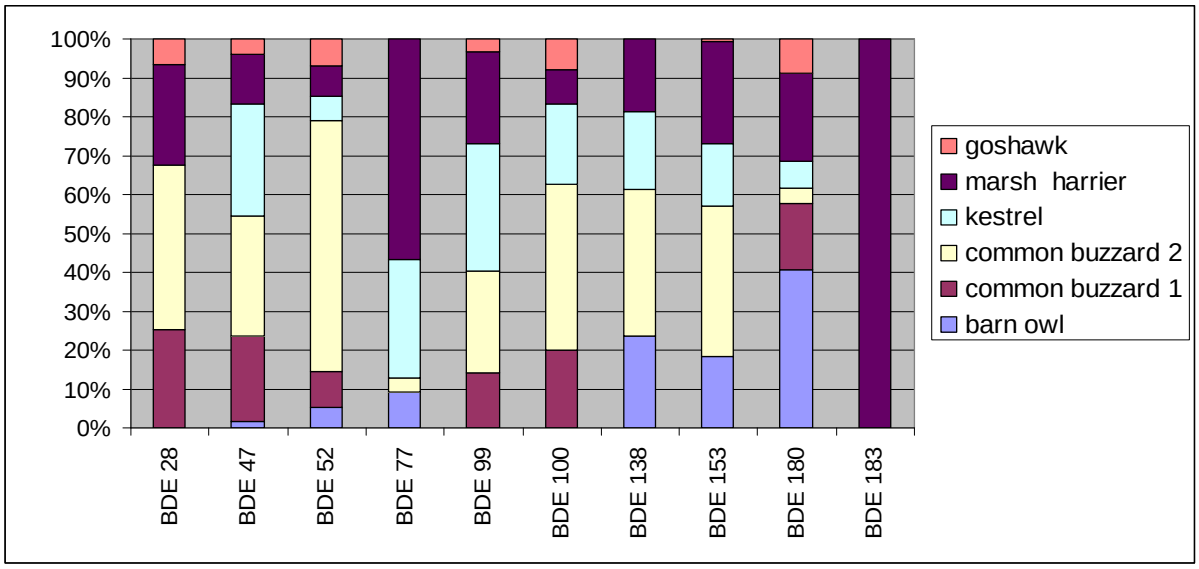

Figure 1. Percentage distribution of the measured PBDE congeners in bird livers.

Results indicate that the highest PBDE levels were found for common buzzard and marsh harrier. It is probably related to their diet, corresponding with their habits and also connected with differences in PBDE congeners accumulation and metabolic capacity.

In most samples, congeners of the two commercial PBDE mixtures (penta- and octaBDE) have been detected with the biggest contribution of pentaBDE one. The obtained in our study concentrations in the bird livers were unexpectedly high compared to available literature data (Jaspers et al. 2006, 2007).

In Poland, PBDEs are not produced and not so widely distributed as inorganic flame retardants. Hence, such high levels could be result from the sampling sites location - near densely populated and heavily industrialized cities or sites contaminated by other POPs. Besides PBDEs, heavy metals and organochlorine pesticides were also analysed, and also detected in significant concentrations, but not reported here.

Conclusions.

All of analyzed PBDE congeners were detected in bird liver samples, with the highest levels of BDE 47, 153 and 99, respectively. This suggests that exposure to these congeners among Polish predatory birds is high. It could be linked with good ability of bioaccumulation and biomagnifications of these congeners. Levels of target analytes was substantially higher than those reported in literature.

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