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DETERMINATION OF BIOACCUMULATIVE BROMINATED FLAME-RETARDANTS AND NATURAL HALOGENATED COMPOUNDS IN EGGS OF NORWEGIAN BIRDS OF PREY

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1 Introduction

In recent years, due to enhanced analytical methods and sophisticated analytical instrumentation, brominated xenobiotics were added to the routineously monitored compounds in the environment. Today, mainly gas chromatographic separation techniques combined with electron capture negative ionisation mass spectrometry detection (ECNI-LRMS) in selective ion monitoring (SIM) using the bromine isotope masses m/z 79 and m/z 81 are used as a sensitive and selective tool to detect organic brominated compounds in the environment. Additionally, high resolution mass spectrometry with electron impact ionisation (EI-HRMS) allowed highly specific detection of the molecule signal for brominated compounds. Thus, brominated flame-retardants have been identified as new environmental pollutants[1]. Brominated flame retardants were recently detected in biota from Norway and the Svalbard archipelago, indicating possible long range transport or local contamination as possible sources[2]. Today it is assumed, that polybrominated diphenyl ethers (PBDEs) belong to the most abundant and persistent group of additive brominated flame-retardants (BFRs). The presence of PBDE in air and biological samples from remote areas of the Arctic indicate a worldwide distribution[3]. Bird species in high trophic levels react very sensitive on relatively low levels of organohalogen compounds, with great compound- and species specific dependency[4]. Due to bioaccumulation, elevated concentration of persistent organic pollutants (POP) can be expected in high trophic level organisms. Therefore, top predating birds are valuable indicator organisms to estimate the influence of antropogenic POPs on this type of ecosystem. BFR were recently detected in substantial amounts in the marine ecosystem, confirming the need of investigating the contamination of top predators as bird of prey with this compound group[4]. Using new analytical detection methods, the presence of hitherto unidentified brominated compounds in Norwegian bird of prey eggs was elucidated. The here presented study intends to contribute with additional scientific information to this rapid developing analytical issue.

2 Material and Methods

A set of 39 eggs of nine different species representing different trophic levels collected from 1991 to 1997 at different nesting sites throughout Norway were routinously analysed for the content of polybrominated biphenyls (PBB) and PBDE (table 1). The analytical method used for the preparation of bird eggs is described in an earlier publication[5]. The following compounds were analysed: PBDE mixture 22 from CIL (#EO-4149) including PBDE 47, 99, 100 and 153; 4,4'-dibromobiphenyl (PBB 15), 2,2',4,5'- and 2,2',5,5'-tetrabrombiphenyl (PBB 49 and 52), 2,2',4,5,5'-pentabromobiphenyl (PBB 101) and 2,2',4,4',5,5'-hexabromobiphenyl (PBB 153). As internal standard ^{13}C-isotope labelled PCB 178 was applied. All isotope labelled standards were purchased from Cambridge Isotope Laboratories (Woburn, MA, USA). Solvents of pesticide grade were employed for sample clean-up and analysis (E. Merck, Darmstadt, Germany).

GC/LRMS-EI quantification of PBB and PBDE:
Routine determination of PBB and PBDE congeners was carried out at the laboratories of the Norwegian Institute for Air Research. A 8560 Mega gas chromatograph (Fisons CE instruments Milan, Italy) was equipped with a 2 m deactivated guard column (J&W, Folsom, CA) coupled to a 30m J&W DB5-MS main fused silica capillary column (0.25 mm id and 0.25 μm film thickness). Helium (He, 5.0 quality) was used as carrier gas at a flow rate of 1 mL/min. The sample extract (2 μL) was injected on-column. The following temperature program was employed: 60 °C, 2 min, 15 °C/min to 180 °C and 5 °C/min to 280 °C, 20 min isothermal. Quantification was carried out with low resolution (LRMS) Finnigan MD800 quadrupole as detector in selected ion monitoring mode (SIM). Electron impact (EI) was used as ionisation method for the determination PBB and PBDE. For the verification of the LRMS results, high resolution measurements (HRMS) with a VG Autospec were used at a resolution of M/ΔM 10,000 and 8000 V acceleration voltage using EI and SIM mode. In both methods the most intensive molecule signals were measured for tri- to heptabrominated congeners.

***GC/ECNI-MS quantification of brominated and natural halogenated compounds*:**
In three selected samples, trace analyses of brominated and natural halogenated compounds were performed at the University of Jena with a HP 5890/5989 MS engine system (Agilent, Palo Alto, CA), using a fused silica column, coated with a ß-BSCD-

phase (BGB 172, BGB Analytik, Adliswil, Switzerland). In the full scan mode, m/z 50-550 (10-40 min) and m/z 50-650 (>40 min) were recorded. In the SIM-mode the Q1- and bromine-selective masses m/z 79, m/z 81, m/z 114-117, m/z 158-161, and m/z 384/386/388 were recorded in two time windows. Other parameters used for quantification were published elsewhere[6]. The GC oven was programmed as follows: 80 °C (isothermal 4 min) to 150 °C (isothermal 2 min), 195 °C (isothermal 1 min), and 230 °C (isothermal 40 min), with heating rates of 20 °C/min between each isothermal plateau.

3 Results and discussion

A variety of PBDE and PBB congeners could be quantified in the analysed samples with capillary gas chromatography coupled to low-resolution mass spectrometry (GC/LR-EIMS). Capillary gas chromatography coupled to high-resolution mass spectrometry was employed for a selected number of samples and confirmed the previous GC/LR-EIMS determination of PBDE and PBB congeners. A variety of PBDE congeners were detected in all egg samples analysed with species dependent differences in the congener distribution patterns. Eggs from Sparrowhawk, Goshawk, White-tailed Sea Eagle and Osprey were higher contaminated with PBDE 47 compared to PBDE 99 and, thus, expressed the typical PBDE pattern documented for biotic samples[3]. Species, mainly feeding on migrating passerines are exposed to contaminants from regions close to potential sources, expressed in a different pattern. Eggs from Peregrine Falcons, Merlins and Gyrfalcons showed a higher proportion of PBDE 99 and 153 compared to PBDE 47. In general, the PBDE and PBB distribution indicates the influence of habitat and food specialisation on the contamination pattern in birds of prey (Figure 1). Sparrow hawk eggs were highest contaminated with PBDE, followed by White-tailed Sea Eagle-, Eagle Owl-, Peregrine Falcon, Goshawk and Osprey eggs (figure 1). Only minor PBDE levels were detected in Golden Eagle, Gyrfalcon and Merlin (between 5 and 40 ng/g ww). The one Eagle Owl egg analysed was relatively high-contaminated. Compared with the technical PBDE mixture "Great Lakes DE 71", Sparrow Hawk, Goshawk and Osprey eggs showed a similar congener pattern, indicating source near contamination. PBB compounds were not as abundant in the analysed egg samples as the PBDE congeners.

Table 1: Bird species selected for the initial BFR survey

Species	Scientific name	Main food objects	No. of samples
1.1.1.1.1 *Merlin*	*3.1.1.1.1.1 Falco columbarius*	Passerines and small waders	3
White-tailed Sea Eagle	*Haliaeetus albicilla*	Fish and seabirds	5
Goshawk	*Accipiter gentilis*	Medium-sized birds, small mammals	7
Golden Eagle	*Aquila chrysaetos*	Mammals and game birds	9
Peregrine Falcon	*Falco peregrinus*	Medium-sized birds	6
Osprey	*Pandion haliaetus*	Freshwater fish	4
Gyrfalcon	*Falco rusticolus*	Medium-sized birds	2
Eagle Owl	*Bubo bubo*	Medium-sized birds and mammals	1
Sparrowhawk	*Accipiter nisus*	Passerines	2

The highest PBB contamination was found in egg samples from Eagle Owl and Sparrowhawk (Figure 1). Sum PBB concentrations, including a variety of unassigned PBB, in eggs of White-tailed Sea Eagle, Peregrine Falcon and Goshawk (average concentration: 40 ng/g ww) were in average ten-times lower compared to PBDE. Only a few eggs of Golden Eagle, Gyrfalcon and Merlin contained measurable amounts of PBB (maximum concentration: 20 ng/g ww). The tetra- and hexabrominated congeners dominated the PBB pattern in the analysed egg samples. No similarities to the pattern of the technical mixture "Firemaster BP6"were found .

Analysis of three eggs from White-tailed Sea Eagle on brominated and natural halogenated compounds with ENCI-MS revealed two bioaccumulative natural halogenated compounds, i. e. Q1 and MHC-1[8]. Q1 was recently characterised as a natural heptachlorobipyrrole derivative in various environmental samples. However, the detection of Q1 in Norwegian egg samples is interesting since Q1 was previously not detectable in Arctic air samples from Spitzbergen[7]. MHC-1 was recently identified as a natural $C_{10}H_{13}Br_2Cl_3$ (monoterpene) component in fish and seals from Europe, Africa, and the Antarctic[7]. In addition, tribromoanisole was identified as a new brominated contaminant in Norwegian bird of prey eggs (Figure 2).

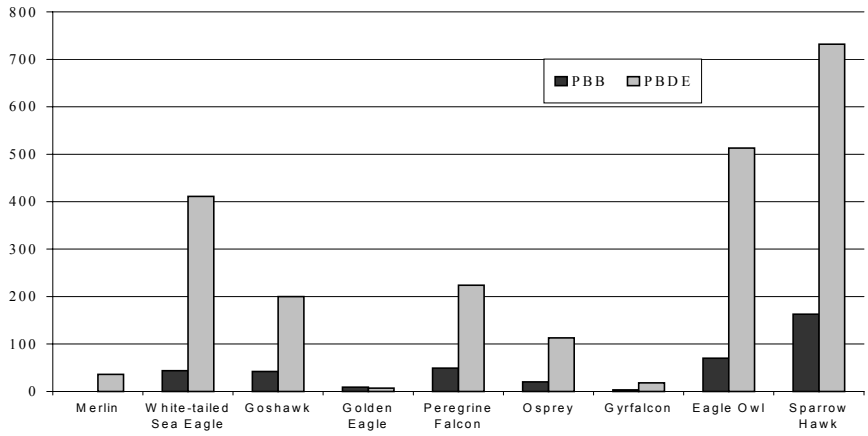

Figure 1: Sum PBB and Sum PBDE concentrations in Norwegian bird of prey eggs (ng/g wet weight).

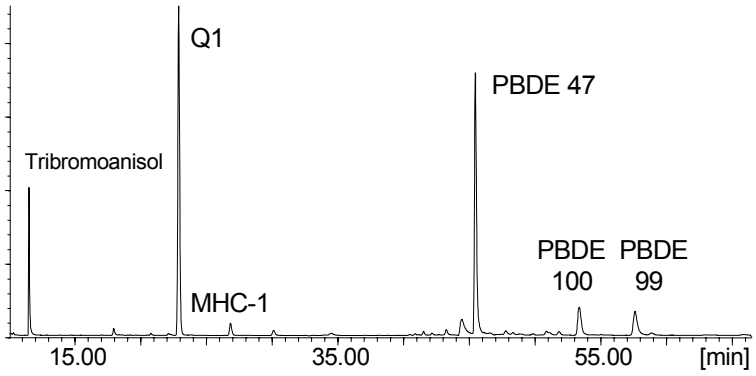

Figure 2: Typical GC/ECNI total ion chromatogram of the new brominated compounds identified in Norwegian White-tailed Sea Eagle eggs.

More details about level distribution, possible sources and environmental consequences will be given in the presentation.

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