# LEVELS AND CONGENER PROFILES OF PBDES IN EDIBLE BALTIC, FRESHWATER, AND FARMED FISH IN FINLAND IN 2009

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## Introduction

The Baltic Sea is a semi-enclosed, shallow area with brackish water and large catchment area, which is why marine organisms are exposed to higher concentrations of many persistent organic pollutants than in larger water bodies. Baltic fish is the major source of many lipophilic environmental pollutants for the Finnish consumers. These include the brominated flame retardants, a diverse group of compounds added to various consumer products to make them less combustible. Polybrominated diphenyl ethers (PBDEs) are a group of 209 congeners that are added to many textiles, furniture, and electronic equipment in such a way that they are not chemically bound to the products. Therefore, they can be leached into the surrounding environment, accumulate to organisms and cause harmful effects, for e.g. endocrine disruptions[1].

In our previous studies, we have observed that PBDE concentrations in fish caught from the northern Baltic Sea, from the Finnish coast, are generally below 5 ng/g fw[2, 3], and that their concentrations have decreased from 1990's levels[4]. Today's levels are in line with studies in central and southern Baltic Sea fish[5].

Here, we report in detail the PBDE concentrations and congener profiles in Baltic, freshwater, and farmed fish in 2009. In addition, inter- and intraspecific differences, as well spatial trends and trophic effects are discussed.

## Materials and methods

Altogether 207 samples (mostly pooled samples of 2–10 individuals) of 17 edible fish species were collected from commercially and recreationally important fishing areas in 2009. The sampling was performed in the Baltic Sea, off the cities of Oulu (n=22), Vaasa (n=5), Pori (n=88, of which 67 were individual herring samples), Turku (n=26), Hanko (n=22), and Kotka (n=25), in three large freshwater areas Lake Inari (n=2), Lake Päijänne (n=4), and Lake Saimaa (n=2), as well as in 11 fish farming facilities (n=11).

The fish species were selected based on their significance in the Finnish diet. The species collected from the Baltic Sea were herring (*Clupea harengus membras*), sprat (*Sprattus sprattus*), salmon (*Salmo salar*), sea trout (*Salmo trutta*), vendace (*Coregonus albula*), roach (*Rutilus rutilus*), perch (*Perca fluviatilis*), pike (*Esox lucius*), pike-perch (*Sander lucioperca*), burbot (*Lota lota*), whitefish (*Coregonus lavaretus*), flounder (*Platichthys flesus*), bream (*Abramis brama*), cod (*Gadus morhua*), and river lamprey (*Lampetra fluviatilis*). From the freshwater lakes, trout, perch, and bream were collected, and the farmed fish species included in this study were rainbow trout (*Oncorhynchus mykiss*), arctic charr (*Salvelinus alpinus*), and whitefish.

During sampling, the length and weight of the fish were determined. The age determination was based on microscopic examination of scales or otoliths. The samples were frozen and kept at -18°C before analysis.

The 15 PBDE congeners analysed were BDE-28, 47, 66, 71, 75, 77, 85, 99, 100, 119, 138, 153, 154, 183, and 209. The analytes were extracted from freeze-dried samples with 15% ethanol/toluene using Accelerated Solvent Extractor ASE-300 from Dionex. The solvent was evaporated and the fat content was determined gravimetrically. Bulk fat was removed using multilayer silica column and sample was further purified on a separate aluminium oxide column. Quantification of PBDEs was performed by Agilent 6890 gas chromatograph coupled to Waters Autospec Ultima high resolution mass spectrometer (GC-HRMS). The column used was DB-5MS (J&W Scientific, 60m, ID 0.25 mm, 0.25 μm) except for BDE-209, for which a respective column of 6 m length was used. The limits of quantification for individual BDE congeners were in the range of 0.22–250 pg/g fw.

## Results and discussion

From the 15 congeners analysed, 10 were detected in over 80% of the samples. BDE-71, 75, 85, and 183 were detected in only 25%, 38%, 0.97%, and 40% of the samples, respectively, and BDE-138 was not detected in any of the samples.

In all of the samples analysed, the $\Sigma_{15}$BDE varied between 0.029–73 ng/g fw (Fig. 1). In some of the samples, BDE-209 was detected in significant proportion: for example in 21 out of 207 samples, BDE-209 accounted for >80% of the $\Sigma_{15}$BDE, and the sum of PBDEs excluding BDE-209 ($\Sigma_{14}$BDE) in all samples varied between 0.029–4.2 ng/g fw. However, in most of the samples, $\Sigma_{15}$BDE was below 5 ng/g fw, and the 25$^{th}$–75$^{th}$ percentile was 0.56–2.6 ng/g fw. This is equivalent to 14–47 ng/g lipid weight (lw). PBDE levels were of similar magnitude than in other studies performed in the Baltic area[5, 6].

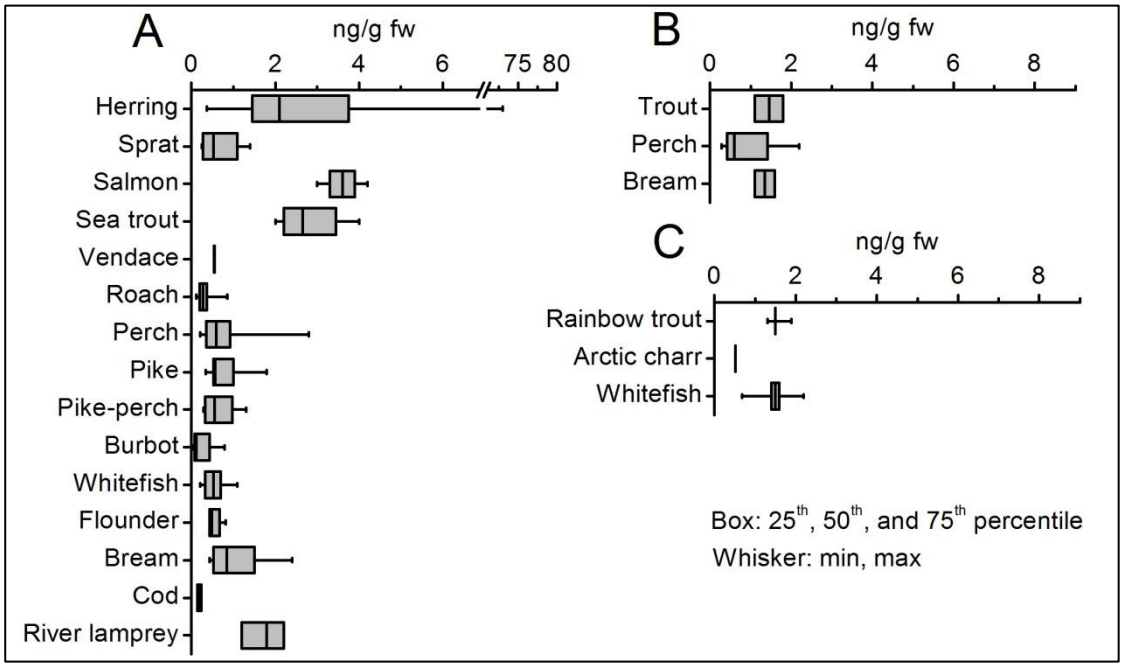


**Figure 1. Sum of 15 PBDE congeners (ng/g fw) in (A) Baltic fish, (B) freshwater fish, and (C) farmed fish.**

The PBDE congeners analyzed in highest proportion were BDE-47, 99, 100, 154, and 209, which is in line with previous studies. However, the contribution of each congener to the $\Sigma_{15}$BDE varied strongly across species (Fig. 2). In all the studied species, the proportions of BDE-47, 99, 100, 154, and 209 varied between 17–67%, 0.38–35%, 4.6–19%, 1.9–12%, 1.1–71%, and 2.5–12%, respectively. The proportion of BDE-209 was particularly high in herring (average 71%), sprat (52%), perch (33%), and pike (23%), caught from the Baltic Sea,

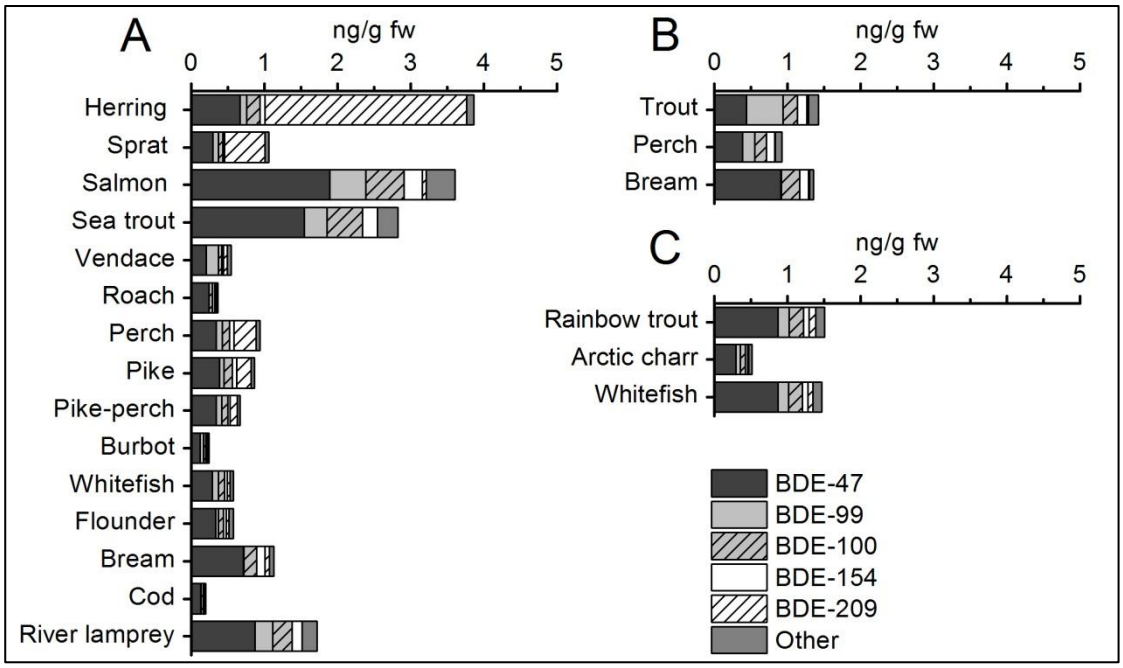


**Figure 2. Average PBDE congener concentrations (ng/g fw) in (A) Baltic fish, (B) freshwater fish, and (C) farmed fish.**

The variation in BDE-209 concentrations was not explained by the age, size, or fat percentage of the fish. If anything, the associations were slightly negative. Among 67 herring individuals caught from the Baltic Sea, off the city of Pori, the Pearson correlation coefficient between BDE-209 and age, length, and fat percentage were -0.21, -0.33, and -0.06, respectively. However, the sum of other 14 BDE congeners increased with both age (r=0.84), length (0.87), and fat pergentage (r=0.26).

The variation in BDE-209 proportion was more likely due to geographical reasons. For example, in herring and perch, the BDE-209 proportion was noticeably higher off the cities of Vaasa and Pori, than other sampling areas, and in sprat, the proportion was higher in the Kotka sampling area (Fig. 3). This suggests regional contamination off the cities of Vaasa, Pori, and Kotka, possibly, but the reason remains to be studied.

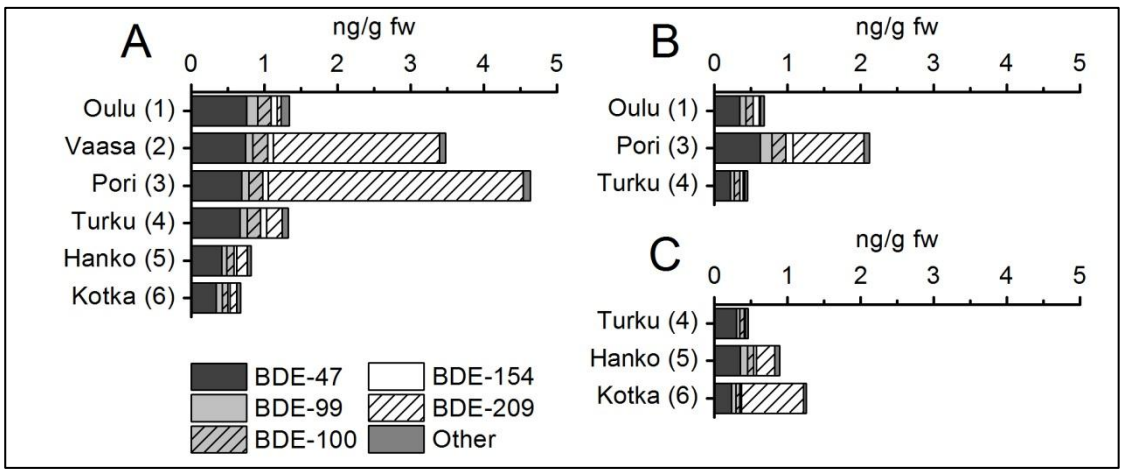


**Figure 3. Average PBDE congener concentrations (ng/g fw) across sampling area in (A) herring, (B) perch, and (C) sprat.**

The results indicate that PBDEs, except for BDE-209, may be bioaccumulated in the marine food chain. This was studied among herring, sprat, salmon, and sea trout, caught from sampling areas with no substantial local BDE-209 contamination (Turku and Kotka). In herring and sprat, the $\Sigma_{15}$BDE was much lower than among their important predators salmon and sea trout (Fig. 4). However, BDE-209 was not present in the predator species while its proportion was significant in the prey species.

Fish are able to debrominate BDE-209 into lower brominated congeners to some extent[7]. Our results are in line with previous studies, indicating that cyprinid fish may be more efficient in debrominating BDEs than other species. For example, the congener profile of the cyprinids roach and bream was different from those of perch; even these species have similar feeding preferences (Fig. 4). In roach and bream, the proportion of BDE-99 was <1% while its proportion in perch was 9.2%. Vice versa, the proportion of BDE-47, the major debromination product of BDE-99, was much higher in roach (66%) and bream (63%) than in perch (36%).

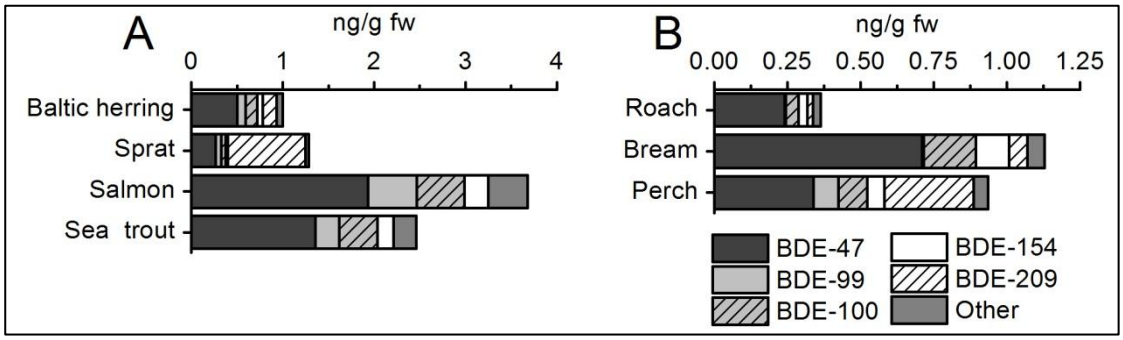


**Figure 4. Average PBDE congener concentrations (ng/g fw) in (A) prey (herring, sprat) and predator species (salmon, sea trout) in Turku and Kotka, and (B) cyprinid (roach, bream) and similar species (perch).**

## Conclusions

Overall, PBDE levels were similar in Baltic, freshwater, and farmed fish. PBDE levels were higher in herring, salmon, and sea trout, and varied substantially between individuals. PBDEs, except for BDE-209, correlated with age, size, and fat percentage of fish, and may bioaccumulate in the marine food chain. There was possible regional contamination in the Baltic Sea, off the cities of Vaasa, Pori, and Kotka, and this should be studied more closely in the future.

## Acknowledgements

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## References

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