Monitoring BFRs in Dutch food from animal origin 2004-2012

Martijn van der Lee*, Stefan van Leeuwen, Ruud Peters and Ron Hoogenboom

Background

Within the Dutch National Plan Residue Monitoring, Dutch food are monitored for a variety of contaminants (e.g. heavy metals, radio-nuclides, halogenated contaminants). Since 2001, dioxins (PCDD/Fs) and dioxin-like polychlorinated biphenyls (dl-PCBs) are monitored in food products of animal origin. PBDEs were added to the program since 2009, HBCDDs and TBBPA have been analyzed since 2011 in a limited number of samples. For PBDEs, HBCDDs and TBBPA, the EFSA risk characterizations [1-4] showed that risks on the exposure to these BFRs is rather limited, with the possible exception of BDE 99. EFSA recommended to perform monitoring of these BFRs in foods, to increase and improve the food safety database on this topic. This poster shows results on BFRs in food for the period 2009 to 2012.

[1] EFSA (2011) Scientific Opinion on (PBDEs) in food. EFSA Journal 9:2156
[2] EFSA (2011) Scientific Opinion on (HBCDDs) in food. EFSA Journal 9:2296
[3] EFSA (2011) Scientific Opinion on (TBBPA) and its derivatives in food. EFSA Journal 9:2477
[4] EFSA (2012) Scientific Opinion on Emerging and Novel (BFRs) in food. EFSA Journal 10:2908

Samples for Dutch National Plan Residue Monitoring

Table 1. Products and number of samples analyzed for BFRs.

Sample origin	n	Meat * n = 304	Milk** n = 48	Egg** n = 93	Liver n = 10	Fish*** n=62
Sheep	74	73			1	
Rabbit	1	1				
Pig	66	60			6	
Horse	4	4				
Chicken	150	57		93		
Goat	1	1				
Deer wild	2	2				
Deer farmed	17	17				
Calf	23	23				
Bovine	118	66	48		4	
Fish	62					62

*) Samples from farmed animals, except wild deer samples. Meat samples were obtained from slaughterhouses. **) Raw milk samples and eggs were obtained from farmers. ***) Fish samples were collected by IMARES, Institute for Marine Resources and Ecosystem Studies. Both wild caught marine fish and farmed fish were obtained from wholesale traders. Eel (6); salmon (6); shrimp (6); herring (5); mussel (4); catfish (3); dab (3); haddock (3); plaice (3); tarbut (3); trout (3); cod (2); hake (2); pangasius (2); sole (2); tilapia (2); whiting (2); crab (1); flounder (1); mackerel (1); red mullet (1).

Method - fat isolation, clean-up and BFR measurements

Before fat extraction, 13C-PBDE209 was added to the samples. Depending on the sample type fat, isolation was done by Smedes or ASE. Fat purification was done using a PowerPrep (FMS). The cleaned extract was concentrated and the recovery standard (13C-PCB209) was added. 10 µl sample extract was introduced into the GCMS (Trace GC, Thermo Finnigan). A 30-meter RTX Cl-pesticide capillary column (ID=0.25mm) was used. Ionization was carried out via NCI using methane as reaction gas. For the HBCDD diastereomers and TBBPA, the fat was also purified on a Powerprep system. The extract was analysed on an LC-ESI-MS/MS system (Micromass Quatro Ultima) using a gradient from 80% eluent A (MeOH, AcN with 0.01% acetic acid) to 85% A, with eluent B being water with 0.01% acetic acid.

Table 2. Validation results for HBCDD diastereomers, TBBPA and PBDEs.

Validation	LOQ ng per gram fat	Trueness (%)	EMU (%)
α-HBCDD:	0.18 ng/g	102	13
β-HBCDD:	0.12 ng/g	100	8
γ-HBCDD:	0.37 ng/g	100	13
TBBPA	0.054 ng/g	97	7
PBDEs	0.005 ng/g	89	38

Sum PBDEs in food from animal origin

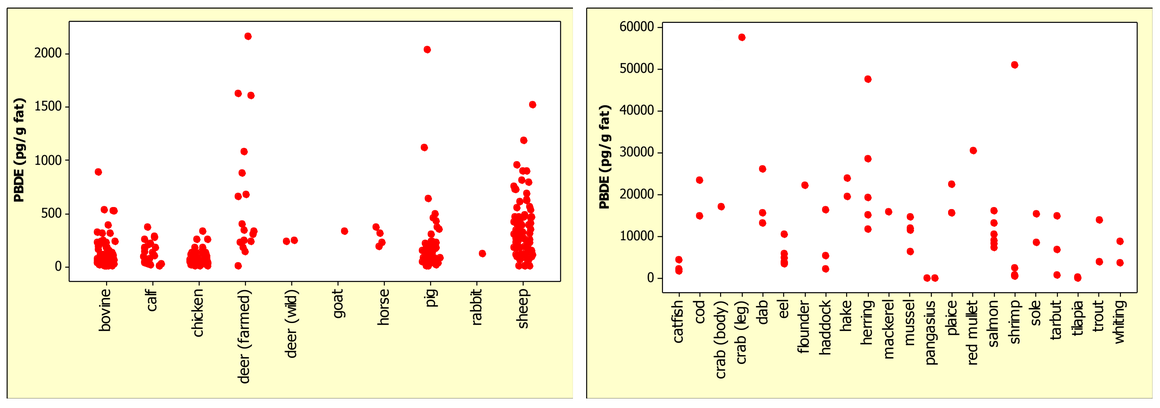


Figure 1. Sum PBDE levels (BDE 17, 28, 47, 49, 66, 71, 75, 77, 85, 99, 100, 119, 138, 153, 154, 183 and 190) in meat and fish (left and right). Sum PBDE based on Lower Bound levels.

All data are expressed on a fat weight basis, showing highest levels for certain fish species. Variation in fish is much larger than in meat, as can be expected since it is a heterogeneous sample group. Levels varied between <LOQ for pangasius to the highest level of about 60000 pg/g fat in a crab leg sample. It should be noted that this high level is caused by the low fat content of crab legs. On a product basis, this sample is among the lowest contaminated samples.

PBDE congener profiles in foods

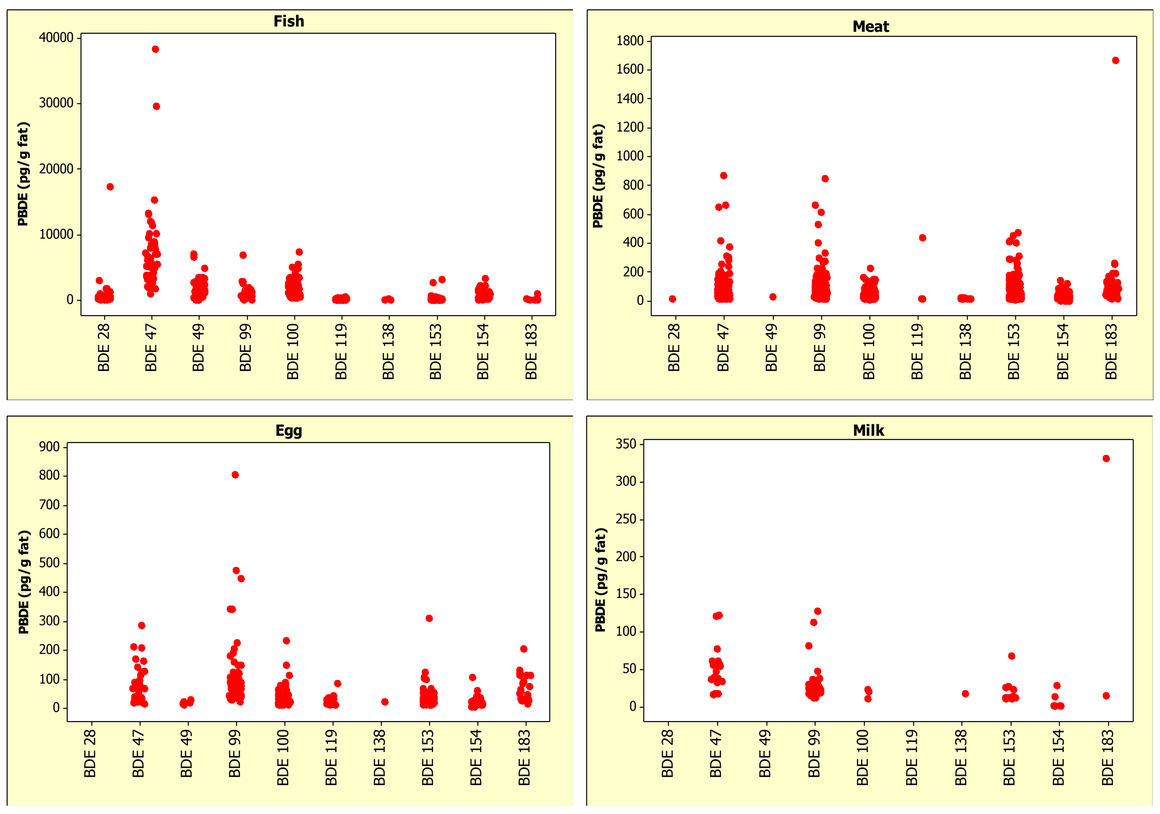
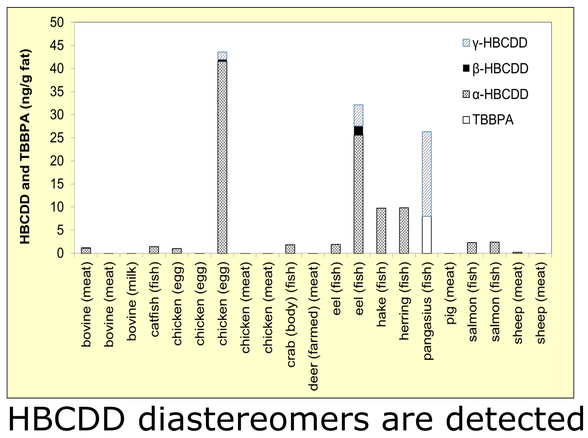


Figure 2. Major PBDE congeners in fish, meat, eggs and milk. Levels <LOQ are not shown.

HBCDD and TBBPA in meat and fish samples



HBCDD diastereomers and TBBPA were analyzed in meat, fish and egg samples. All fish samples were farmed fishes. TBBPA was detected in pangasius at 8 ng/g fat and twice at just above the LOQ in other samples. The origin of the TBBPA and α-HBCDD in pangasius is unknown. HBCDD diastereomers are detected more frequently. Fish and egg samples showed the highest levels and contamination frequencies. One egg sample contained a level of HBCDDs up to 44 ng/g fat (not shown). In these food samples α-diastereomer dominated over β- and γ-diastereomer.

RIKILT Wageningen UR
P.O. Box 123, 6700 AB Wageningen, The Netherlands
Contact: Martijn.vanderLee@wur.nl
T + 31 (0)317 480299
www.wageningenUR.nl/en/rikilt

Acknowledgement
This research was financed by the Dutch Ministry of Economic Affairs.