Brominated flame retardants in eggs – data from Kazakhstan and Thailand

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Introduction

Eggs have been found to be sensitive indicators of PCDD/F and PCB contamination in soils and are an important exposure pathway from soil pollution to humans. Eggs from contaminated areas can readily lead to exposures which exceed thresholds for the protection of human health [1-3]. Chickens and eggs might therefore be considered ideal "active samplers" and indicator species for POPs contaminated sites but there are, as yet, few systematic studies linking pollution sources, related exposures and concentrations of contaminants in eggs.
While there are a range of studies on PCDD/Fs and PCBs in eggs [e.g. 1-7], there are only a few studies assessing brominated flame retardants (BFRs) in chicken eggs [7-11]. Furthermore, most studies have been conducted in Europe with less data are available from developing countries and countries with economies in transition. In this study, we sought to broaden the available data and eggs were sampled at sites suspected of being impacted by POPs in Kazakhstan and in Thailand and the relationship between the potential sources and contamination levels has been examined. This issue has gained further significance as it was established in a UK food survey that polybrominated dibenzo-p-dioxin and dibenzofurans can also contribute significantly to total dioxin exposure for the UK population [12]. This is possibly linked to the UK having set exacting flammability standards for furniture and thus having been a major user of brominated flame retardants including polybrominated diphenyl ethers (PBDEs).
While often mainly PBDEs or hexabromocyclododecane (HBCDD) are screened as BFRs in environmental monitoring and in monitoring of food and feed, today a wide range of other BFRs and CFRs are used as flame retardants in products. Therefore in this study in addition to PBDEs and HBCDD also some other novel BFRs have been analysed for their presence in chicken eggs from Kazakhstan and Thailand.

Materials and methods

Free range egg samples were collected from five locations in Kazakhstan. These samples included chicken eggs from small-scale farms in Balkhash city, Baskuduk, Shetpe and Tauchik. Eggs from one supermarket in Karaganda were analysed to help establish background levels.
In Thailand free range eggs were sampled in two locations (Map Tha Put city and the island of Koh Samui). In addition, one sample was bought from a supermarket in Bangkok.
Selected brominated contaminants measured in eggs included polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCDD), hexabromobenzene (HBBz), pentabromoethylbenzene (PBEB), 1,2-bis(2,4,6-tribromo-fenoxy) ethane (BTBPE), octabromotrimethylphenyl indane (OBIND) and decabromodiphenyl ethane (DBDPE). Pooled samples of individual egg samples were collected at each of the selected sites in order to obtain a representative sample. The size of samples was from 3 to 10 eggs. The fat content of the respective pool samples was determined and BFR levels recalculated to fat content.
The identification and quantification of the analyte was conducted by gas chromatography coupled with tandem mass spectrometry with detection in electron ionization mode. Ultra-high-performance liquid chromatography

coupled with tandem mass spectrometry detection (UHPLC–MS/MS) was used for the analysis of HBCDD. The analysis was conducted in a Czech certified laboratory (The University of Chemistry and Technology, Department of Food Chemistry and Analysis; Prague, Czech Republic).
The analytes were extracted by a mixture of organic solvents hexane/dichloromethane (1:1). The extracts were cleaned by gel permeation chromatography (GPC).

Results and discussion

Levels of POP-BFRs (PBDE and HBCDD) in eggs

Selected brominated flame retardants (BFRs) including POPs (PBDEs and HBCDD) and novel BFRs were measured in chicken eggs at the various locations. Of all BFRs reported in the analysis, PBDE and HBCDD were the two BFRs with highest detection frequency and with the highest detection level (see Table 1).
For HBCDD one highly impacted sample was detected with 18320 ng/g fat in free range chicken eggs (4 pooled eggs) from Shetpe sampled in 2016. In the locality of Shetpe car wrecks were located with chickens feeding around them and this could have served as potential source of contamination. HBCDD was used in cars as flame retardants for textiles, mats and expanded polystyrene (EPS) and extruded polystyrene (XPS) parts [13]. The HBCDD level in eggs (3 pooled eggs) from a second small-scale chicken farm in Shetpe contained 430 ng/g fat which also indicated an exposure source.
The second highest HBCDD level (1036 ng/g fat) was detected in eggs (6 pooled eggs) from the supermarket in Karaganda. The farms where the eggs were produced were not assessed. Since eggs from a supermarket normally originate from chickens in battery farms or stables, indoor sources of HBCDD might be responsible for the contamination. The other BFRs were low in the eggs sampled in the supermarket with PBDEs levels of 9.5 ng/g fat indicating no other specific BFR source at the farm where the eggs originated.
In Baskuduk, the eggs were sampled from a part of the town close to large waste landfill. The HBCDD levels (187 ng/g fat) and PBDE levels (28.1 ng/g fat) were elevated. Also these eggs were the only sample were BTBPE were detected at level of 3.46 ng/g fat. This indicate that the landfill might have some impact on BFR exposure.
The locations in Thailand where eggs were sampled from free range chicken included Map Ta Phut which adjoins a large industrial estate in Rayong Province where large petrochemical facilities operate and Koh Samui, an island off the east coast whose economy is dominated by tourism and subsistence agriculture. Furthermore one sample were taken from Bangkok supermarket produced from caged chickens.
All three pooled egg samples from Thailand showed relatively low BFR contamination levels. Only the pooled egg samples from Map Ta Phut had HBCD level of 165 ng/g while for the other pooled eggs PBDEs and HBDD were below 5 ng/g fat (Table 1).

Levels of some novel BFRs in eggs

The flame retardant decabromodiphenyl ethane (DBDPE) is a major brominated alternative for DecaBDE. In this study the levels of this compound were below the relatively high detection limits (2.7 to 10 ng/g fat) in all analysed samples (Table 1). This indicates that DBDPE is not present at relevant levels at the assessed sites. DBDPE was also below detection limit in some other studies in chicken eggs in UK [14] and falcon eggs in Spain [15] while it was detected in falcon eggs in Canada [15].
Hexabromobenzene, pentabromoethylbenzene and octabromotrimethylphenyl lindane were below detection limits in all samples indicating a low relevance for exposure of these compounds for the assessed sites in Kazakhstan and Thailand. HBBz was also not detected in chicken eggs in the UK [14].
The BFR 1,2-bis(2,4,6-tribromo-fenoxy) ethane (BTBPE) was detected in several samples below and around 1 ng/g (Table 1). The highest BTBPE level was 3.46 ng/g in Baskuduk in the vicinity of a landfill (Table 1).

Table 1: Brominated flame retardants in chicken eggs sampled in Kazakhstan and Thailand (in ng/g fat).

Locality	Balkhash-south-west A	Balkhash-south-west B	Balkhash-Rem-baza	Balkhash-Rem-baza	Karaganda-supem.	Baskuduk	Shetpe	Tauchik	Map Tha Put (Thailand)	Koh Samui (Thailand)	Bangkok-super-market (Thailand)	Qihua (China)
Sum of PBDEs**	3.51	25.8	234	16.0	9.50	28.10	n.d.	n.d.	3.03	3.30	0.92	3.10
Sum HBCD	<2.1*	197	<2.6*	225	1036	187	18321	430	143.5	165.4	<2.8*	<3.3*
HBBz	<0.16*	<0.20*	<0.20*	<0.22	<0.21*	<0.33*	<0.31*	<0.01*	<0.01*	<0.16*	<0.21*	<0.26*
PBEB	<0.16*	<0.20*	<0.20*	<0.22*	<0.21*	<0.33*	<0.31*	<0.01*	<0.01*	<0.16*	<0.21*	<0.26*
BTBPE	0.16	<0.20*	<0.20*	<0.22*	0.29	3.46	<0.31*	<0.01*	1.07	0.27	<0.21*	<0.26*
OBIND	<1.33*	<1.70*	<1.70*	<1.80*	<1.79*	<3.27*	<3.27*	<0.1*	<0.1*	<1.35*	<1.77*	<2.16*
DBDPE	<2.66*	<3.40*	<3.40*	<3.60*	<3.57*	<6.54*	<6.29*	<10.0*	<10.0*	<2.70*	<3.55*	<4.31*

*** below LOQ ** Following congeners were analyzed: BDE 28, BDE 47, BDE 49, BDE 66, BDE 85, BDE 99, BDE 100, BDE 153, BDE 154, BDE 183, BDE 196, BDE 197, BDE 203, BDE 206, BDE 207 and BDE 209**

Conclusions

The high HBCDD and elevated PBDE levels in some pooled egg samples in Kazakhstan indicate exposure pathways of BFRs to eggs and humans. The areas where old car wrecks were stored indicates that chickens are possibly picking materials containing flame retardants such as polyurethane or polystyrene or textiles which over time were scattered in the areas surrounding end of life vehicles which are stored for long time or are recycled. These contaminants are distributed over soil in areas where car wrecks are stored or processed.

With PCDD/PCDF it was found that soil contamination is highly relevant for exposure. Therefore, the Low POPs Content for materials which might end up in soil (e.g. ashes from biomass or waste burning) need to be low. For BFRs the exposure to BFR containing materials seems a relevant exposure pathway. Therefore, exposure pathways like insulation foam in stables or areas were flame retarded materials are stored or disposed, need to be secured so that chicken and other food producing animals do not have access. POP-BFRs and other flame retarded materials should be better managed along the life cycle and requirements of the Stockholm and Basel Convention should be met. This should apply, in particular, for countries with limited management and technical capacity to deal with of end of life vehicles and hazardous household waste. The use and production exemptions recently granted via the Stockholm Convention for DecaBDE in car parts and in textiles should be further assessed for the potential to increase human exposure either directly or via the food chain as demonstrated in the egg scenario.

In addition, the exposure relevance of PBDEs, HBCDD and other BFRs in soil should be better assessed to understand their relevance at industrial sites where BFR containing wastes are thermally treated in metal industries with potential releases.

The emerging BFRs analysed in this study were below detection levels or showed low levels as has been found also in other egg studies indicating a current minor relevance of these compounds in respect to exposure pathway via chicken eggs.

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