BROMINATED DIOXINS (PBDD/Fs) IN FREE RANGE CHICKEN EGGS FROM SITES AFFECTED BY PLASTIC WASTE

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Introduction

Free-range chicken eggs are sensitive indicators of POPs contamination in soils/dust and represent an important human exposure pathway[1-3]. As "active samplers" they can be used to reveal POPs contamination, particularly in areas impacted by polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs; "chlorinated dioxins" in brief) and polychlorinated biphenyls (PCBs)[4-8], as well as by brominated flame retardants (BFRs)[9-12]. This study aims to investigate brominated dioxins in free range chicken eggs sampled at sites close to sub-standard plastic waste disposal locations in developing countries.

Polybrominated dibenzo-p-dioxins and dibenzofurans (PBDD/Fs; "brominated dioxins" in brief) are known to be byproducts of commercial PBDE mixtures since 1986[13]. They were also found to be byproducts of some novel BFRs like DBDPE[14] or BTBPE[15-16]. PBDFs have also been found to be formed by sunlight exposure during normal use, as well as during disposal/recycling processes of flame-retarded consumer products[17]. Some studies found PBDD/Fs in copper metal recycling[18], in the air around a waste incinerator plant[19], around an open burning site[20], and, recently, in children's toys[21]. PBDD/Fs have been found to exhibit similar toxicity and health effects as their chlorinated analogues (PCDD/Fs)[22-26]. They can, for example, affect brain development, damage the immune system and fetus, or induce carcinogenesis[25]. "Both groups of compounds show similar effects, such as induction of aryl hydrocarbon hydroxylase (AHH)/EROD activity, and toxicity, such as induction of wasting syndrome, thymic atrophy, and liver toxicity"[23].

With the broad use of BFRs in many applications, the question has arisen about the presence of PBDD/Fs in the food chain, as they are persistent and bioaccumulative and found in different environmental compartments[25]. The WHO expert panel has concluded that PBDD/Fs and some dioxin-like polybrominated biphenyls (dl-PBBs) may contribute significantly to daily human exposure to the total dioxin toxic equivalencies (TEQs)[26]. In general, PBDD/Fs are less regulated than PCDD/Fs. For example, PBDD/Fs are not currently listed under the Stockholm Convention[27]. There is littledata available on their presence in the environment compared to PCDD/Fs. Recent studies in China, Japan, Taiwan or Vietnam demonstrate that PBDD/Fs are widely present in Asia[28-31]. IPEN and Arnika recently found PBDD/Fs in consumer products from recycled e-waste plastic sold worldwide[32].

There is also very little information about their presence in food and/or consumer products, and whether they have direct impacts on human health, including in vulnerable groups such as children and women of childbearing age, particularly in developing countries where regulations and standards to control PBDD/Fs in food or waste incineration emissions are lacking.

Materials and methods

In this research, fifteen pooled samples of free-range chicken eggs (from 14 hot spots around the world) and two reference samples from supermarkets (see Table 1) were analyzed for PBDD/Fs in the MAS laboratory, Muenster, Germany. The accredited method MAS_PA002, ISO/IEC 17025:2005 was used to determine PBDD/Fs. The basic steps of the analyses can be summarized as follows:

- Addition of $^{13}C_{12}$-labelled PBDD/F internal standards to the sample extract
- Multi-step chromatographic clean-up of the extract
- Addition of $^{13}C_{12}$-labelled PBDD/F - recovery standards
- HRGC/HRMS analysis
- Quantification via the internal labelled PBDD/F-standards (isotope dilution technique and internal standard technique).

All egg samples were also analyzed for PCDD/Fs and dl PCBs by HRGC-HRMS at the laboratory of the State Veterinary Institute in Prague, Czech Republic. Toxic equivalency factors from the 2005 World Health Organization reevaluation of dioxins and dioxin-like toxicity[26,33] were used for the calculation of levels in TEQs so that the contribution of PBDD/Fs to overall dioxin toxicity of each sample is known.

Table 1: Overview of samples of chicken eggs

Country	Activity	Locality	Sample ID	Month/year of sampling	*n* eggs in sample	Fat (%)
Belarus	Recycling, pre-recycling	Gatovo	Gatovo	06/2014	3	15.4
Cameroon	Dumpsite	Yaoundé - Etetak Q.	YA-3	08/2018	6	14.3
Gabon	Waste incineration	Nkoltang	GA-E-NKOL	11/2019	5	13.6
Gabon	Dumpsite	Libreville - Ozounge	GA-E-OZOU	11/2019	5	11.2
Ghana	Waste yards / e-waste site	Agbogbloshie	AGB-E	12/2018	4	14.7
Ghana	Ref	Accra (supermarket)	ACC-M-E	12/2018	6	8.8
China	Waste incineration	Wuhan	Wuhan 2	09/2014	3	12.5
China	Waste incineration	Wuhan	Wuhan 1	03/2014	6	15.5
China	Ref	Beijing	Control	10/2014	3	10.1
Indonesia	Waste yards / e-waste site	Tangerang	SEM-E-1	11/2019	3	16.2
Indonesia	Waste incineration	Tropodo	TROP-E-1	10/2019	6	13.9
Indonesia	Metallurgy	Kendalsari	KEN-E-1/19	11/2019	6	14.3
Kenya	Waste yards / e-waste site	Nairobi – Ngara m.	KE_002	01/2020	6	16
Mexico	Recycling, pre-recycling	Guadalajara	GUDAL-EGG1	04/2019	5	14
Philippines	Waste yard / e-waste site	Bagong Silang	PH-E-1-2	09/2019	2	13.8
Tanzania	Dumpsite	Pugu Kinyamwezi	TZ-PU-KI_EGG	01/2020	9	18.0
Thailand	Waste yards / e-waste site	Samut Sakhon	Samut Sakhon	02/2015	3	11.6

Results and discussion

Concentrations of PBDD/Fs and PCDD/Fs plus dl PCBs in pooled egg samples in this study are summarized in Table 2. PBDD/Fs levels in eggs above LOQ are also presented in the graph at Picture 1.

Table 2 Results of analyses

Activity	Locality	Sample ID	PBDD/Fs	PCDD/Fs + dl PCBs
			(pg TEQ g^{-1} fat)	
RE/E-w	Guadalajara	GUADAL-EGG1	5.4	5.9
RE/ELVs	Gatovo	Gatovo	<LOQ	16
WY/E-w	Tangerang	SEM-E-1	6.9	72
WY/E-w	Bagong Silang	PH-E-1 and 2	11	20
WY/E-w	Samut Sakhon	Samut Sakhon	16	96
WY/E-w/ELVs	Accra – Agbogbloshie	AGB-E	300	856
WY/E-w	Nairobi - Ngara market	KE_002	8.5	502
WI	Tropodo	TROP-E-1	0.33	172
WI	Wuhan	Wuhan 2	<LOQ	13
WI	Wuhan	Wuhan 1	27	16
WI	Nkoltang (MedWI)	GA-E-NKOL	< LOQ	15
DU	Yaoundé-Etetak Quart.	YA-3	0.17	13
DU	Libreville – Ozounge	GA-E-OZOU	2.0	21
DU	Pugu Kinyamwezi	TZ-PU-KI_EGG	3.0	35
ME	Kendalsari	KEN-E-1/19	0.57	60
Ref	Beijing (supermarket)	Beijing (superm.)	<LOQ	0.48
Ref	Acrra –supermarket	ACC-M-E	< LOQ	0.56

RE – recycling and pre-recycling; E-w – electronic waste; ELVs – end of life vehicles; WY – waste yards; WI – waste incineration; DU – dumpsite; ME – metallurgy; Ref – reference sample; LOQ = 1.4 - 3.8 pg TEQ g^{-1} fat

The highest level of PBDD/Fs were measured in eggs from Agbogbloshie, an e-waste and ELVs scrapyard followed by eggs from the vicinity of waste incinerators in Wuhan (27 pg TEQ g^{-1} fat). The observed high PBDD/Fs levels in eggs from Samut Sakhon (16 pg g^{-1} fat), Bagong Silang (11 pg g^{-1} fat), Tangerang (7 pg g^{-1} fat) and Guadalajara (5 pg g^{-1} fat) can be explained by e-waste plastics being dismantled or shredded and/or openly burned at some of these sites. PBDD/Fs are already present in e-waste plastics as by-products in BFRs[34,21], and they are also released as unintentionally produced chemicals formed as a result of burning plastics treated with BFRs. The level of 300 pg TEQ g^{-1} fat from Agboglboshie is the highest ever measured level of PBDD/Fs in eggs globally. A previous study reported a level of 62 pg TEQ g^{-1} dw in soil sample near the eggs sampling site in Agboglboshie[35].

The eggs from Wuhan had higher levels of TEQs originating from PBDD/Fs compared to PCDD/Fs and dl-PCBs. The level of PBDD/Fs in TEQs concentration was equal to the sum of PCDD/Fs in eggs from

Guadalajara, the site where e-waste plastic is recycled into new products. High levels of PBDEs and novel-BFRs of 31 and 379 ng g^{-1} respectively, were measured in the recycled plastic produced at this site[36]. E-waste plastic is shredded at this site that might explain the potential pollution of the soil or dust with PBDD/Fs that are subsequently ingested by free range chickens.

Two samples from supermarkets in Accra, Ghana and Beijing, China and three pooled free-range eggs from Gatovo, Belarus, Wuhan 2, China and Nkoltang, Gabon had levels below the laboratory limit of quantitation (LOQ).

A report from Ireland showed levels of 0.244 – 0.415 pg TEQ g^{-1} fat of PBDD/Fs in eggs[37]. That is two orders of magnitude lower than the levels measured in free-range chicken egg samples from Wuhan or Samut Sakhon, and three orders of magnitude lower than in the samples from Agbogbloshie. However, the levels of PBDD/Fs in egg samples from Tropodo, Yaoundé – Etetak Q., and Kendalsari are similar to those measured in Ireland. It seems that lower levels of PBDD/Fs were generated in the vicinity of aluminum smelters (Kendalsari, Indonesia) and/or dumpsites in one of the African cities where dumping and burning of BFRs containing wastes was probably not involved to such an extent as, for example, at e-waste sites or larger dumpsites. Low levels of PBDD/Fs in eggs from Tropodo are hard to explain as very high levels of PBDEs were found in the same sample coming from an area affected by burning plastic waste as fuel in tofu factories[38-39].

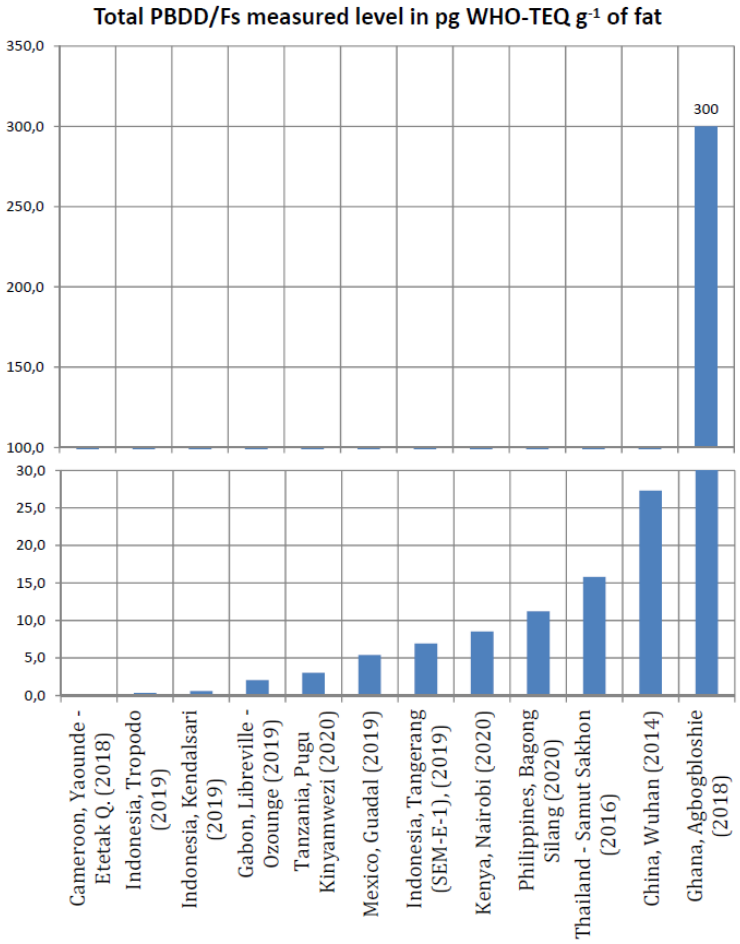

Figure 1 Levels of PBDD/Fs measured in the samples

In the parallel research, we monitored also other POPs, including PCDD/Fs and dl-PCBs (see the results in Table 2) for comparison with levels of PBDD/Fs. Part of the research included calculation of dietary intake of selected POPs through consumption of free-range chicken eggs. In some cases, brominated dioxins contribute significantly to the total TEQ levels in the egg samples and at the same time to the dioxin exposure of the human body, in particular for the egg samples from sites affected by e-waste[23], because those plastics have originally been treated with BFRs. This is mainly the case for the samples from Agbogbloshie, Wuhan, Tangerang, Samut Sakhon, Bagong Silang, and Guadalajara.

Conclusion

This study demonstrated that sub-standard settings of e-waste plastic disposal and metal smelting plants are growing sources of PBDD/Fs releases to the environment in developing countries. PBDD/Fs are also shown to contribute significantly to overall dioxin toxicity of eggs. All the sources of these toxic substances and their precursors must be eliminated or strictly controlled at national, regional and global level.

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