

POPs contamination at 'recycling' and metallurgical site in Thailand

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Introduction: This study evaluates the results of the analyses for Persistent Organic Pollutants (POPs) in the free-range chicken eggs in a vicinity of the artisanal recycling workshops in Samut Sakhon, a neighboring province of Bangkok, Thailand. Free-range chicken eggs were used for monitoring levels of POPs contamination at certain places in many previous studies⁽¹⁻⁷⁾. Eggs have been found to be sensitive indicators of POPs contamination in soils or dust and are an important exposure pathway from soil pollution to humans. Thus eggs from contaminated areas can lead to significant POPs exposures that exceed thresholds for the protection of human health⁽⁷⁻¹⁰⁾.

Chickens and eggs might, therefore, be ideal 'active samplers' and indicator species for evaluation of the POPs contamination level of sampled areas, particularly by polychlorinated dibenzo-*p*-dioxins, furans (PCDD/Fs) and polychlorinated biphenyls (PCBs)⁽⁷⁾. Based on this assumption, the free-range chicken eggs were collected in February 2015 and used in this study as one of the monitoring tools, to analyze for the selected POPs, i.e., PCDD/Fs, PCBs, polybrominated dibenzo-*p*-dioxins and furans (PBDD/Fs), polycyclic aromatic hydrocarbons (PAHs), and brominated flame retardants (BFRs). This study discovers serious contamination within the food chain by various POPs in Samut Sakhon and the level of these chemicals measured in the eggs is the second highest level ever measured in chicken eggs globally⁽⁷⁾. We also looked at levels of POPs found in other environment compartments sampled in Samut Sakhon in addition to free range chicken eggs.

The data and analysis of free-range chicken eggs was also already summarized in the broader context of samples from other industrial hot spots in Thailand⁽¹¹⁾, as well as POPs found in samples of soils, sediments and biota from the same sites⁽¹²⁾ within the joint EARTH and Arnika project "Increasing Transparency in Industrial Pollution Management through Citizen Science".

Materials and Methods: Two pooled free-range egg samples were collected close to the artisanal recycling workshops in Samut Sakhon Province in central Thailand. One pooled sample of eggs (SMSK 2015) was taken in February 2015 on the yard in a small artisanal recycling facility. The other sample of eggs (SMSK 2016) were taken in February 2016 in an area with a high concentration of small-scale metal smelting and recycling facilities. Each selected site was determined in order to be a representative sample. The third sample was bought from a supermarket in Bangkok as the control sample in this study. The size of each representative sample was three eggs, while the control sample was six eggs.

The selected POPs like PCDD/Fs, PCBs, and PAHs were analyzed by the GC-HRMS at Axys Varilab, an accredited laboratory in Vrane nad Vltavou, Czech Republic. The fat content of the current pool samples was determined and pollutant levels recalculated to fat content in the analysis.

The content of pentachlorobenzene (PeCB), hexachlorobutadiene (HCBd) and BFRs were also analyzed. The identification and quantification of the samples were analyzed by the gas chromatography coupled with tandem mass spectrometry 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 HCBd. The analysis was conducted in a certified laboratory at 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 the gel permeation chromatography (GPC).

Analyses of fish, soil and sediment samples were done in the same laboratories by using same methods as for the eggs. The extraction method should be matrix specific.

Results and Discussion: *Levels of PCDD/Fs and PCBs;* Both egg samples from Samut Sakhon exceeded the EU maximum level set for PCDD/Fs and dioxin-like PCBs (dl-PCBs), expressed as WHO-TEQ in chicken eggs⁽⁸⁾. The background levels for PCDD/Fs and dl-PCBs which were measured in the chicken eggs from a supermarket in Bangkok were 0.08 and 0.001 pg WHO-TEQ/g fat, respectively. The highest level of dioxins (84.04 pg WHO-TEQ/g fat) and dl-PCBs (11.67 pg WHO-TEQ/g fat) (see Table 1), were

measured in the eggs sampled in the area of a small artisanal recycling facility where metal was also reclaimed from waste after it went through the process of on-site open burning. Another egg sample, collected from an area close to 'recycling' facilities of the secondary metal production was also found to exceeding the level of the EU standard for dioxins in eggs.

Levels of PBDD/Fs: The eggs sampled in Samut Sakhon in February 2015 were also analyzed for PBDD/Fs. Level of these chemicals measured in these eggs was between 15.8 – 22.9 pg WHO-TEQ/g fat. It was, to our knowledge, the second-highest level measured in chicken eggs globally. The highest level of 27.3 – 29.2 was measured in the free-range chicken eggs sampled near a municipal waste incinerator in Wuhan, China ^(13,14).

Levels of Polycyclic Aromatic Hydrocarbons (PAHs): The level of PAHs found in the egg sample from Samut Sakhon (SMSK 2016) was 2730 ng/g fat, which is ten- fold the level in eggs from the Bangkok supermarket, and it was second highest level of PAHs measured in egg samples collected at Thai hotspots. A higher level was observed only in a sample from Saraburi ⁽¹¹⁾. The potential source of egg contamination was the secondary production of metals or open-air burning of waste in the area that hens used to breed.

Levels of BFRs: The high level of PBDEs (426.89 ng/g fat) was measured in the eggs sample from an area close to 'recycling' facilities of the secondary metal production. Levels of BFRs in free range chicken eggs from different hotspots in 17 countries were described in the IPEN report. The maximum level of HBCD (160 ng/g fat) in free-range chicken eggs was observed in the sample from Dandora landfill in Nairobi in that study. The eggs from Samut Sakhon reached the same level of HBCD. Almost the same level was also observed in eggs from Koh Samui, however much higher levels were recently found in eggs from Kazakhstani hotspots and a supermarket ⁽¹⁵⁾.

The highest level of PBDEs (107 ng/g fat) in the IPEN report was observed in the sample from the vicinity of a hazardous waste incinerator in Turkey ⁽¹⁶⁾. The sample from Samut Sakhon had more than four times higher level of PBDEs than maximum found in the IPEN study.

Table 1. Persistent organic pollutants in chicken eggs sampled in Samut Sakhon Province, Thailand

Sample	SMSK 2015	SMSK 2016	Bangkok- supermarket	EU standard / limits
PCDD/Fs (pg/g fat)	84.04	6.2	0.08	2.5
dl-PCBs (pg/g fat)	11.67	6	0.001	-
Total PCDD/Fs + dl-PCBs (pg/g fat)	97.5	12.23	0.08	5.0
PBDD/Fs (pg/g fat)	15.8	-	-	-
Sum of 16 PAHs (ng/g fat)*	-	2730	233	-
Sum of PBDEs (ng/g fat)**	-	426	3.10	-
Sum of HBCD (ng/g fat)***	-	159	<LOQ	-

Notes: *16 PAHs is sum of naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, benzo(ghi)perylene, and dibenzo(a,h)anthracene; **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; *** HBCDs is sum of isomers α -HBCD, β -HBCD, and γ -HBCD.

Dietary intake of POPs in eggs from Samut Sakhon: It was noted that the egg samples received in 2016 were breeding eggs of fighting roosters, not generally used as food; therefore, it was simply used for a biomonitoring tool to represent the potential exposure of local inhabitants. The egg sample in 2015 was normally kept for family consumption as food in which the most critical levels of POPs were found. Levels of PCDD/Fs, DL PCBs and PBDD/Fs from samples in Samut Sakhon were far too high in comparison with most of the samples collected in other countries during a new round of free-range chicken eggs sampling organized by IPEN and Arnika ^(7,13,17,18). Just by eating approximately half an egg from the sample collected in the artisanal recycling facility area, one should exceed the suggested maximum level of daily intake of PCDD/Fs and dl-PCBs ^(19,20) at least twice even without the inclusion of comparably toxic PBDD/Fs into this calculation. These levels are far too high when we take into account that PCDD/Fs and dl-PCBs are contained in other food as well ⁽¹⁸⁾.

POPs in other environmental compartments of Samut Sakhon: The POPs PCDD/Fs, PCBs and PAHs were also measured in samples of soil samples taken in the neighborhood of an artisanal waste recycling workshop (SMSK soil 2) and small nonferrous metallurgical plant (SMSK soil 1) in Samut Sakhon. Also fly ash from a coal power plant reprocessed for production of casting molds in another workshop in Samut Sakhon was analyzed. The highest level of PCDD/Fs, 35-times higher than the reference level for Thailand, was observed in the area of secondary metallurgical production plant. The level next to the waste 'recycling' workshop where the eggs (SMSK 2015) were sampled was high, more than 12-fold the reference level for PCDD/Fs. Fly ash samples contained a high level of PAHs as did samples from the area of the metallurgical plant. All results are summarized in Table 2. Reference site levels were used from a Swedish EPA study ⁽²¹⁾.

Table 2. Persistent organic pollutants in soil and fly ash sampled in Samut Sakhon Province, Thailand

Sample	SMSK soil 1	SMSK soil 2	SMSK fly ash 1	Ref. site ²¹
PCDD/Fs (pg/g dw)	35.2	12.8	1.9	0.68 – 1.0
dl-PCBs (pg/g dw)	5.72	0.001	0.27	0.022 – 0.028
Total PCDD/Fs + dl-PCBs (pg/g dw)	40.92	12.8	2.17	0.70 – 1.0
6 i-PCBs (ng/g dw)	1.2	1.06	NA	NA
Sum of 16 PAHs (ng/g dw)	1,747	488	3,210	NA

Conclusions: This study demonstrates some emerging problems of pollution by POPs in relation to the small-scale smelting and recycling areas in Thailand. It discloses important contamination throughout the food chain by many POPs in Samut Sakhon Province, especially in a dense area of small-scale smelting and artisanal 'recycling' factories, which quite often had open-burned waste, including e-waste, to reclaim metals. These facilities are common sources of unintentionally produced POPs²² as well as BFRs. To prevent further releases of these chemicals in Samut Sakhon, it would require better organization and regulation of the facilities in this locality. Some of these facilities should be replaced by more appropriate and clean technology for recycling. Moreover, it would require assistance from the state and responsible authorities to both improve the recycling industrial practices and monitoring of POPs contamination to prevent health risks. Importantly, this area should be included among other actions into the updated NIP for the Stockholm Convention on POPs.

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