CONTAMINATION OF BACKYARD CHICKEN EGGS BY DIOXINS, FURANS AND DL-PCBS CAUSED BY AN UNCONTROLLED FIRE IN DISPOSABLE TIRES

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Brief description of background and the aim of the study

A fire hit a cement factory in the city of Vespasiano, located in the metropolitan area of Belo Horizonte (Brazil) on the morning of August 20, 2014. The fire reached an open area of the company where tires were stored to be burnt in furnaces. The co-processing of tires in cement industry is a common practice for waste disposal. Gaseous emissions from controlled burning process are usually contaminated with dioxins, furans and other impurities, but at very low levels (<0.50 ng/m^3).[1] In the aforementioned uncontrolled fire event, however, the flames reached very high heights and the smoke spread throughout the neighborhood regions. Although the flames could be managed during the same day, small fires continued to appear for two more days. It is reasonable to suppose that this unrestrained fire has generated dioxins, furans and PCBs-dl and that the smoke has contaminated the local soil. Hence, because free range backyard chickens will probably be contaminated upon soil ingestion. Thus to verify the extension of contamination, and taking into account that PCDD/Fs and dl-PCBs accumulate preferentially in the fatty fraction of foods, this paper aims to monitor the level of these toxic compounds in free-range backyard chicken eggs.

Materials and methods

Eggs were collected weekly from the same supplier, located about 1 km away from the event, for a period of eight weeks. The first sampling was made in the second week after fire. Samples from the fifth and sixth weeks were analyzed together. In each collection, at least 3 eggs were chosen, which were stored in a refrigerator until analysis. The edible part (yolk and egg white) of the eggs collected in the same week was joined to form a single sample. An isotope dilution method for quantification of 17 polychlorinated dioxins (PCDDs) and furans (PCDFs) in and 12 dl-PCBs was conducted. Briefly, the method uses pressurized liquid extraction (PLE) followed by clean up steps (elution of extracts into two sequential columns filled with distinct stationary phases: acid silica-gel and Florisil®) and gas chromatography coupled with high resolution mass spectrometry (GC-HRMS) analysis. $^{13}C_{12}$-labelled PCDD/Fs and dl-PCBs were used as internal and injection standards. The method was validated according to the European Commission, as described in the regulations 2012/252/EU and 2011/1259/EU. More details about the procedure adopted herein are provided in one of our previous work.[2]

Results and discussion

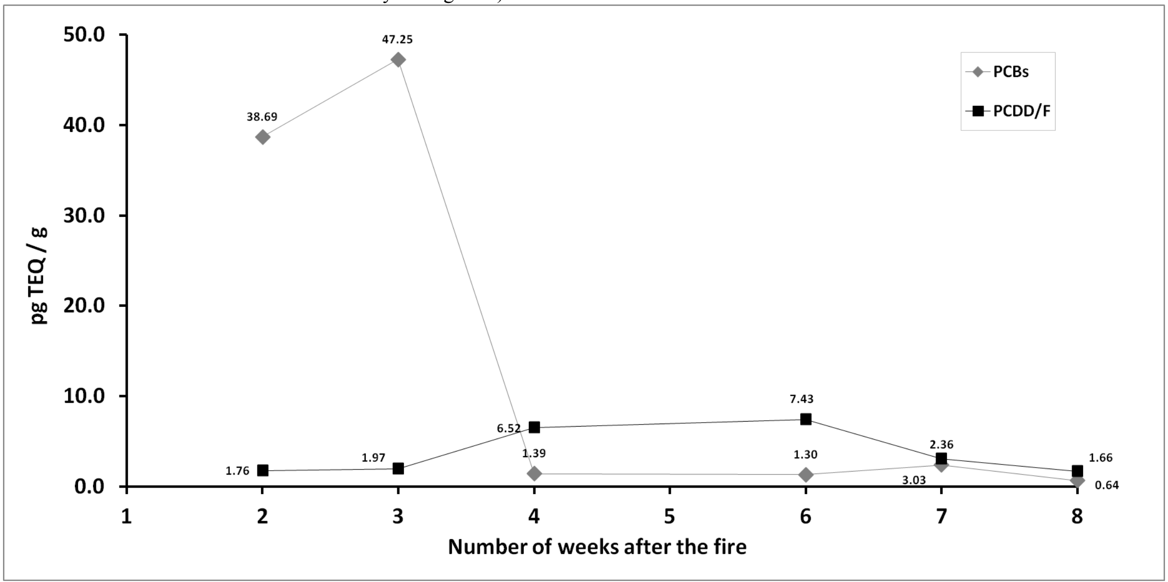
Data displayed in **Table 1** show that among the 29 compounds analyzed in the first sample (collected after two weeks of fire occurrence), 19 congeners were detected above the limit of quantification (LQ). Of the 17 congeners of PCDD/Fs, only 7 were higher than the LQ. When analyzing all samples, among PCDD/F, the highest concentration was found for OCDD (18.8 pg/g fat). All PCBs-dl were also found, presenting the mono-ortho PCBs the highest levels. Highest concentration were quantified for PCB-118 (66,415 pg/g fat). For the non-ortho PCBs, the highest concentration levels were for PCB-77 (1,148 pg/g fat). The highest total TEQ value was found at the sample collected in the third week after the fire: 49.23 pg/g TEQ (upperbound, fat basis). This value is eight times higher than the maximum permitted level adopted by the European legislation[3], i. e. 5.0 pgTEQ/g fat. The mon-ortho PCB-126 (at 35.12 pg/g TEQ) was the congener that most contributed to the high total TEQ value.

Table 1. Concentration (in pg/g) of each congener (PCDD/Fs and dl-PCBs) over time (in weeks). Values in fat content.

Analyte	Week 2 Conc. (pg/g)	Week 3 Conc. (pg/g)	Week 4 Conc. (pg/g)	Week 6 Conc. (pg/g)	Week 7 Conc. (pg/g)	Week 8 Conc. (pg/g)
2,3,7,8-TCDF	1.50	1.79	5.73	5.59	0.96	0.98
2,3,7,8-TCDD	<0.25	<0.25	0.88	1.04	0.27	<0.25
1,2,3,7,8-PeCDF	<0.70	0.89	6.15	6.70	1.76	0.94
2,3,4,7,8-PeCDF	1.17	1.35	5.16	5.55	1.88	1.17
1,2,3,7,8-PeCDD	0.67	0.77	1.92	2.26	0.96	<0.50
1,2,3,4,7,8-HxCDF	0.74	0.76	5.70	6.62	2.43	2.21
1,2,3,6,7,8-HxCDF	<0.50	<0.50	3.31	4.13	1.46	0.92
2,34678-HxCDF	<0.50	<0.50	1.21	1.99	1.57	0.84
12,3,4,7,8-HxCDD	<0.50	<0.50	0.67	0.76	0.95	<0.50
1,2,3,6,7,8-HxCDD	1.36	1.46	1.63	2.00	1.36	0.75
1,2,3,7,8,9-HxCDD	<0.50	<0.50	0.68	0.85	1.24	<0.50
1,2,3,7,8,9-HxCDF	<0.50	<0.50	<0.50	<0.50	1.30	<0.50
1,2,3,4,6,7,8-HpCDF	<1.25	<1.25	1.92	2.49	2.04	<1.25
1,234678-HpCDD	6.52	5.75	4.10	3.78	2.55	2.11
12,3,4,7,8,9-HpCDF	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25
OCDD	18.80	13.31	11.20	6.12	6.03	4.72
OCDF	<2.50	<2.50	<2.50	<2.50	<2.50	<2.50
PCB-81	31.72	46.22	<12.50	<12.50	13.43	<12.50
PCB-77	576.56	1.148.41	30.38	31.06	23.49	<17.41
PCB-126	351.22	434.25	12.74	12.00	18.95	5.61
PCB-169	8.30	9.42	3.10	2.75	13.84	1.30
PCB-123	558.02	755.60	<250	<250	<250	<250
PCB-118	63157.05	66415.36	<250	<250	843.44	774.94
PCB-114	1252.21	1346.38	<250	<250	<250	<250
PCB-105	23367.17	25163.07	<250	<250	368.44	373.08
PCB-167	10125.11	10080.73	<250	<250	<250	<250
PCB-156	8023.74	8170.42	<250	<250	<250	<250
PCB-157	1725.76	1761.37	<250	<250	<250	<250
PCB-189	261.26	<250	<250	<250	<250	<250
PCDD/F Upperbound TEQ-WHO (pgTEQ/g)	1,76	1,97	6,52	7,43	3,03	1,66
dl-PCBs Upperbound TEQ-WHO (pgTEQ/g)	38,69	47,25	1,39	1,30	2,36	0.64
Total Upperbound TEQ-WHO (pgTEQ/g)	40.46	49.23	7.90	8.73	5,39	2.31

It is noticeable that the contamination profile of each congener changed over time. The OCDD concentration decreased over the weeks. It is also noticeable that excepting for OCDD and 1,2,3,4,6,7,8-HpCDD, the PCDD/Fs concentrations increased over the weeks, reaching a maximum level at the sixth week after fire. Unlike the PCDD/Fs, the PCBs reached their maximum levels at the third week after fire and their concentrations decreased afterwards. These data are presented in **Figure 1** and probably indicate that the excretion time is different for both classes of compounds thus revealing that the chicken organism may metabolize them via quite distinct metabolic routes.

Figure 1. TEQ values for dl-PCBs and PCDD/F in eggs over the weeks after the fire (samples from the fifth and sixth weeks were analysed together).



Conclusions

The results displayed herein indicate that the occurrence of an uncontrolled fire came to contaminate free-range eggs from chickens that lived about 1 km away from the event. The maximum degree of contamination was verified at the third week after fire, in a level of 49.23 pg/g TEQ (upperbound, fat basis). On the lollowing weeks, contamination decreased substantially, reaching 2.31 pg/g TEQ (upperbound, fat basis) at the eighth week, less than the maximum permitted level .

Acknowledgements

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References

1. BRAZIL, RESOLUÇÃO CONAMA nº 316/2002

2. Augusti, D.V., Magalhães E.J., Nunes, C.M., dos Santos, E.V., Prates, R.G. and Pissinatti, R. (2014) *Anal. Methods*, **6**, 1963-1969.
3. EC. (2011). COMMISSION REGULATION (EU) No 1259/2011 of 2 December 2011amending Regulation (EC) No 1881/2006 as regards maximum levels for dioxins, dioxin-like PCBs and non dioxin-like PCBs in foodstuffs. *Official Journal of the European Union*(320), 18-23.