BUILDING RELATED SOURCES OF PCBS IN EGGS FROM FREE RANGE HENS

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Introduction

At present most food products are compliant with the EU maximum levels (MLs) for dioxins (PCDD/Fs) and PCBs and it seems difficult to apply risk-based monitoring. Some food products more frequently exceed the limits, like wild eel but also mitten crabs from certain rivers, sheep livers and eggs from free-range chickens. For this reason, the EU recommended additional monitoring on these products.

In the Netherlands the issue on eggs from free-ranging hens was discovered in 2001 on a relatively small farm[1]. Follow-up studies showed that soil must be the major source, although the levels were low and much lower than existing limits for certain applications. More eggs were examined and confirmed that in part of the free-range eggs the levels could exceed existing MLs. Similar was observed in other countries, also in the case of private owners[2]. Additional carry-over studies confirmed the good absorption of dioxins and PCBs from soil and that intake of rather low soil levels could already result in increased levels in eggs[3]. This can be explained by the concentration of these contaminants into a small amount of egg fat (5 g/egg).

With respect to potential sources, some cases have been described in literature where the contamination of was caused by a neighboring company, like in the case of a wood-preserving company in Oroville, California, applying pentachlorophenol[4]. In Brescia, Italy, a PCB-producing plant caused the contamination of surrounding farms[5]. However, there are no other cases described in literature, where the contamination came clearly from outside the farm, although one might expect that some of the older waste incinerators, before being improved, could have been responsible for such cases. Also certain fires could in principle cause such contaminations, depending largely on the materials that are burnt. Similar might be expected if chickens would forage in polluted river banks, but this seems not to occur in practice.

A study was carried out to further examine the situation on commercial organic farms, including potential measures to overcome the problems[6]. This showed e.g. that in particular the smaller farms show the highest levels. Measures like removal of fire sites, feeding inside the stable, reduced time of foraging outside, were advised to farmers to deal with the problem. In addition self-control programs were introduced for free-range egg producers, prescribing that every flock of chickens has to be checked at several weeks after being introduced at the farm. Depending on the level, follow-up controls are obligatory. This self-control showed that levels in most samples are now well below the MLs. However, during the past years a number of farms reported problems and follow-up actions were started to reveal the source of the contamination. This paper describes a number of these recent incidents in particular with elevated PCB-levels and as a result also PCDFs.

Materials and methods

Samples were analysed by GC/HRMS for PCDD/Fs and PCBs by routine methods applied at RIKILT. Egg samples were extracted using the ASE 350 (Dionex, USA) with hexane/acetone (1:1) as extraction solvent. For soil the same procedure using the ASE 350 was applied, however with toluene/ethanol as the extraction solvent. Soil samples were spiked prior to extraction with ^{13}C labeled standards , while for the egg samples the obtained fat was spiked with the ^{13}C labeled standards. All extracts were purified using the automated PowerPrep™ system (FMS). The clean-up resulted in the collection of two purified fractions, one with mono-ortho dl-PCBs and non-dioxin-like PCBs and the other with dioxins and non-ortho dl-PCBs.

The fractions were concentrated using the Power-Vap (FMS) and analyzed by GC-HRMS using an Agilent (Wilmington, USA) gas-chromatograph 6890N (GC column DB5 MS 60m, 0.25mm i.d., 0.25µm; J&W, Folson, USA) and an AutoSpec Ultima high resolution mass spectrometer (Waters, Milford, USA) operated in electron impact ionization mode using selected-ion monitoring and controlled by Masslynx data system. GC-HRMS data were processed using DIOXNOP software to determine the concentrations and subsequently the TEQ levels, based on WHO-TEFs 2005. The performance of the methods is regularly checked by participation in PT-tests.

In the case of PCDD/Fs, congener patterns are expressed as relative contribution to the PCDD/F-TEQ to suppress the contribution of the higher chlorinated congeners. In the case of PCBs all 12 dioxin-like and 6 non-dioxin-like PCBs were combined. For dl-PCBs PCB 126 in all cases contributed for more than 90% to the TEQ level. In addition, the congener patterns in the source were corrected for the carry-over rates in laying hens by multiplying the levels with the CORs described previously[3]. Subsequently the levels were summed and the relative contribution calculated.

Results and discussion

Use of building debris

In 2011 an egg sample tested positive in the Dutch control programme on animal derived products. Levels based on the WHO-TEFs 1998 were 1.5 and 7.4 pg TEQ/g fat for PCDD/Fs and dl-PCBs, and 96 ng/g fat for the 6 ndl-PCBs (MLs were 3 and 6, but no ML for the ndl-PCBs). The farm participated in the previous studies of Kijlstra et al.[4], showing rather low levels. Since then, a new stable was built. Soil was sampled at various locations in the courtyard showing elevated levels of both dl- and ndl-PCBs close to the stables. This part contained a lot of building debris that had been used to fortify the soil before building the new stable. Debris was analysed showing levels of 9.6 and 35.1 ng TEQ/kg dm (TEFs 1998) for PCDD/Fs and dl-PCBs, and 450 µg/kg dm for the 6 ndl-PCBs. Figure 1 shows the patterns for PCDD/Fs and PCBs in the building debris, as compared to the eggs. When comparing these patterns it is important to take into account the carry-over of the different congeners. PCBs 52 and 101 e.g. are not really excreted in eggs, probably due to metabolism, especially once the source is removed. This feature can actually be used to evaluate whether the source is still present.

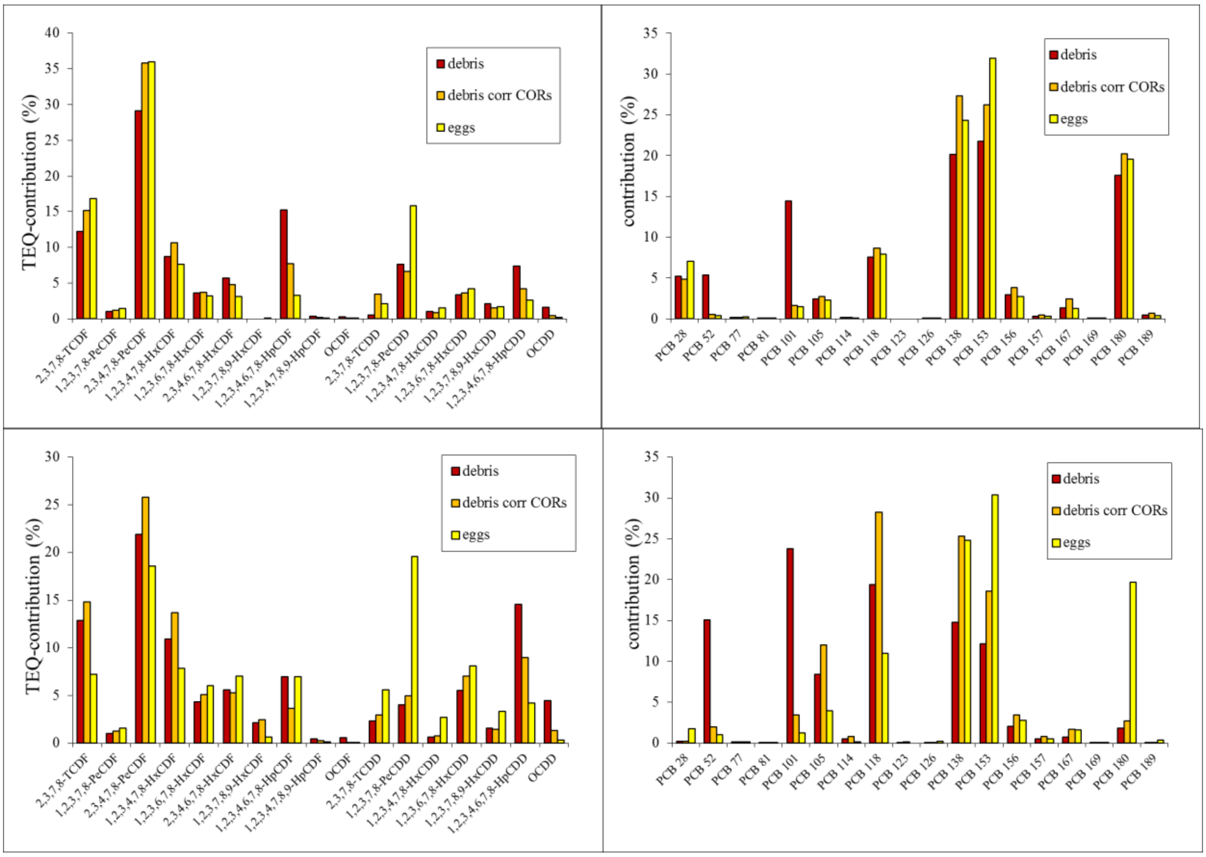

Figure 1. Congener patterns for PCDD/Fs (left) and dl- and ndl-PCBs (right) in building debris and eggs from farms 1 (upper panels) and 2 (lower panels). In addition the source pattern was corrected for the carry-over rates.

The farmer was advised to keep the hens inside resulting in a gradual decrease of the levels, but overall the farm could not deliver eggs for about 2 months. The relatively long period was partly caused because initially the litter/soil inside the stables was not removed. The soil near the stables was covered with concrete and clean sand before hens were allowed outside again.

A second case started after a notification beginning of 2012, because of elevated dl-PCB levels in eggs. The farm was visited and samples were taken from the 3 stables. PCDD/F levels were 2.0, 2.4 and 1.3 pg TEQ/g fat (new ML 2.5) and for the sum of PCDD/Fs and dl-PCBs 14.9, 6.8 en 7.5 pg TEQ/g (new ML 5). The levels of ndl-PCBs were also elevated, but were low when compared to the first farm, being 27, 18 and 17 ng/g fat (new EU-ML 40). Also this farm had participated in previous studies[4], showing low contamination. Recently, new soil was introduced into the courtyard after removal of asbestos that had been used in the past for fortifying the soil. To facilitate the work for the trucks, building debris had been applied in the courtyard. Analysis of this material showed levels for PCDD/Fs and dl-PCBs of 2.4 and 18.0 ng TEQ/kg dm and for the 6 ndl-PCBs of 573 µg/kg dm. Figure 1 (lower panels) shows a comparison of the congener patterns with a reasonable comparison, especially after correction for the CORs. The eggs showed a larger contribution of the higher chlorinated congeners PCBs 153 and 180, more similar to what was observed on the first farm. This difference between eggs and debris might be explained by variation in the congener patterns in the debris. Three weeks after the first visit, laying hens were kept inside and after another 4 weeks the levels in all 3 stables were just below the MLs, but still exceeded the ALs for dl-PCBs. The latter is of concern because certain retailers apply even lower limits. Eventually, the contaminated soil was replaced.

Roof plates

In October 2012, another farm reported problems, this time a farm raising young hens. Based on the elevated levels in eggs from a customer that received laying hens from this farm, it was shown that the fat of the young hens (not yet laying eggs) was highly contaminated, in particular with dl- and ndl-PCBs. The stable was actually divided into two parts, one with white hens and one with brown hens, which foraged on the courtyard on either side of the stable. PCDD/F levels in the body fat were respectively 4.2 and 1.9 pg TEQ/g fat, for the sum of PCDD/Fs and dl-PCBs 238.3 and 82.3 pg TEQ/g and for the ndl-PCBs 469 and 169 ng/g fat.

Based on new rules the young hens had to be able to forage outside. Further investigations on the farm showed that especially the soil close to the walls, was highly contaminated. In the absence of a gutter, the suspicion was on the roof which contained asbestos plates that contained some kind of coating, originating from the beginning of the seventies. Analysis of swab samples and rasp from the roof confirmed the presence of high PCB levels. Figure 2 (upper part), shows the patterns of the soil (without/with correction for the CORs), and the body fat of the white and brown hens, showing an excellent match. Similar was true for the first eggs collected from the two types of hens, showing levels for PCDD/Fs of respectively 1.7 and 0.6 pg TEQ/g fat, for the sum of PCDD/Fs and dl-PCBs of 79.0 and 19.4 pg TEQ/g fat and for the ndl-PCBs 115.0 and 36.5 ng/g fat. Egg levels decreased gradually, but nevertheless it was decided to kill the white hens because it took too long to decrease the levels below the MLs. The difference in the levels between the two types of hens was reflected in the soil levels and could be explained by the fact that on the side of the brown hens, new soil had been applied recently. Total TEQ levels in soil were around 70 and 400 ng TEQ/kg dm on the brown and white hens side.

End of 2013, a similar problem was discovered on another farm with free ranging hens. The one year old hens had gone through a moulting period and had just started to lay eggs again. During this moulting period they were kept inside. The farm was visited and egg samples taken from various stables. Only the eggs from one of the four stables contained levels above the ML, being 12.9 pg TEQ/g fat for the sum of PCDD/Fs and dl-PCBs, as compared to 0.6 pg TEQ/g fat for the PCDD/Fs and 18.3 ng/g fat for the ndl-PCBs. Based on the known half-life, it was decided to remove the hens in the contaminated stable from the farm, also to guarantee that there was no mixing with eggs from the other stables.

The courtyard used by hens from this stable was adjacent to a barn with an old roof, also from the beginning of the seventies and again without any gutters. Soil collected from the area where the water ran down, contained high levels of PCDD/F and PCBs with a highest observed level of 13.5 and 654.3 ng TEQ/kg dm for PCDD/Fs and total TEQ and 1918 µg/kg dm for ndl-PCBs. Figure 2 (lower panels) shows the congener pattern for the eggs as compared to those from the soil, before and after correction for the CORs. In the case of the

PCDD/Fs, the comparison was not as good as observed in other cases, with some clear contribution of TCDD and PeCDD. This might be explained by the relatively low PCDD/F TOQ-levels in the eggs. The pattern from the soil is again typical for PCBs with a high contribution of the PCDFs. The PCB-pattern in soil and eggs was very similar, especially after correction for the CORs. The pattern was not exactly the same as in the case of farm 3, with a relatively higher contribution of PCB 101 and smaller contribution of PCB 180.

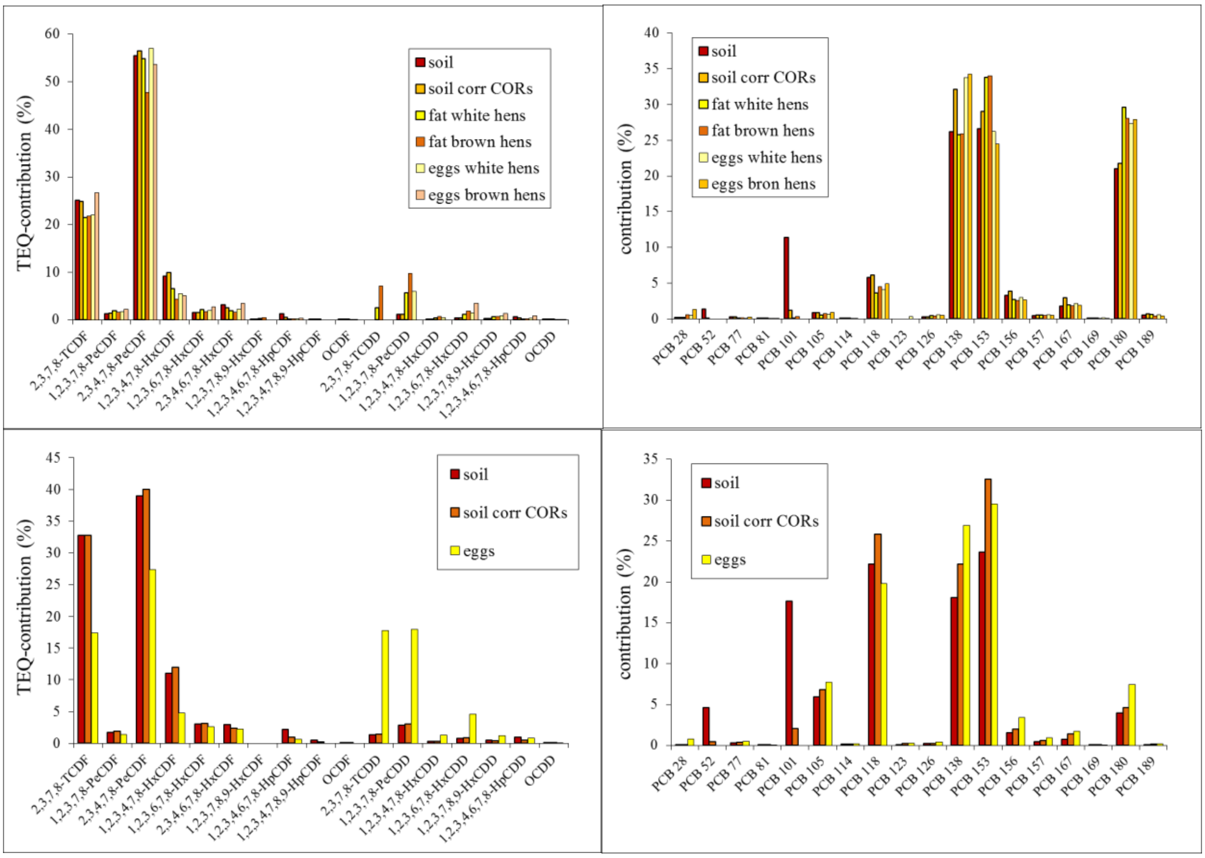

Figure 2. Congener patterns for PCDD/Fs (left) and dl- and ndl-PCBs (right) in soil and eggs from farms 3 (upper panels) and 4 (lower panels). In addition the source pattern was corrected for the carry-over rates.

Conclusions

The cases described above confirm that a contamination coming from within the farm is in most cases the more likely source. Special attention should be paid to the presence of former fireplaces but also old building materials and roofs. This source of PCBs seems to have been underestimated in measures to remove these compounds from the food chain. When comparing congener patterns, the inclusion of carry-over rates is rather helpful.

References:

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