DIOXINS IN ORGANIC EGGS DUE TO CONTAMINATED CORN

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Introduction

A number of food and feed incidents have occurred with dioxins and dioxin-like PCBs during the past decade. Some of these incidents were detected due to the EC policy with respect to these contaminants, the setting of limits and the increased monitoring. In most cases these incidents, once detected, were solved within a relatively short time, thus preventing the exposure of consumers above critical levels. Other issues seem more structural like fish from polluted rivers. Another issue is the intake of contaminated soil by animals foraging outside. It has e.g. been shown that even low levels of dioxins and dl-PCBs in soil may result in increased levels in the eggs of hens foraging on these soils (1,2). In order to reduce the levels, a number of measures were advised to farms with free-ranging chickens, like inside feeding, reduced foraging time and increased awareness of sources that might contaminate the foraging area. This resulted in much lower levels in the eggs. The present paper describes a very recent incident with organic eggs that turned out to be food-related due to the contamination of organic corn imported from the Ukraine.

Description of the incident

At the end of March, RIKILT detected in a routine monitoring program an egg with an elevated level of dioxins. The sample first showed up positive in a screening assay and was subsequently confirmed by GC/HRMS to contain a dioxin level of 10.9 pg TEQ/g fat, i.e. 3.5 times over the EU maximum limit for dioxins of 3 pg TEQ/g fat. In this case the sample also exceeded the maximum level for the sum of dioxins and dl-PCBs. The pattern was marked by a high contribution of TCDF and the two PeCDFs to the TEQ-level (Figure 1). The sample also contained slightly elevated levels of PCBs but far below the current EU action limit for dl-PCBs or proposed EU maximum limit for indicator PCBs. The sample turned out to be taken at the beginning of March at a small farm with organic laying hens and as such seemed related to the well-known problem of elevated dioxin levels in especially eggs from small organic farms.

At about the same time, however, RIKILT was contacted by a large company exporting, among others, organic eggs to Germany. Since a number of years, the farms producing eggs exported to Germany are under a very strict control programme (KAT), applying a limit for dioxins of 2 pg TEQ/g fat, i.e. similar to the EU action limit. Recently a number of farms had shown increased levels and as a result were blocked. However, additional research on these farms did not reveal the source. The pattern in the eggs was however identical to the one observed in the eggs analysed by RIKILT. Further evaluation showed that the feed was derived from the same feed company. As a result it was concluded that the feed must have been the source. Interestingly, the pattern resembled that presented in a recent EU rapid alert (RASFF), issued half of March and dealing with contaminated vitamin A palmitate. Although a likely source, there were some doubts whether this could have been the source, based on the percentage of such ingredients in feed, and also regarding the fact that the premixes used for the feed had been checked and were negative for PCDD/Fs.

Follow-up actions

Fortunately, one of the farmers found to be positive in the KAT-program, had taken samples from all the charges of feed that he obtained since the beginning of December. Four of these samples were analysed by RIKILT and three of them showed elevated dioxin levels around 0.88 to 1.04 ng TEQ/kg, slightly above the EU maximum limit of 0.75 ng TEQ/kg for dioxins. The first sample, obtained at the beginning of December was negative, but subsequent samples from half of December till the end of January were positive. The pattern was again very similar to that in the eggs, including the PCBs. A feed level around 1 ng TEQ/kg may seem rather low but previous studies by RIKILT showed that feeding of laying hens with such a feed for several weeks will result in elevated dioxin levels in the eggs (3,4).

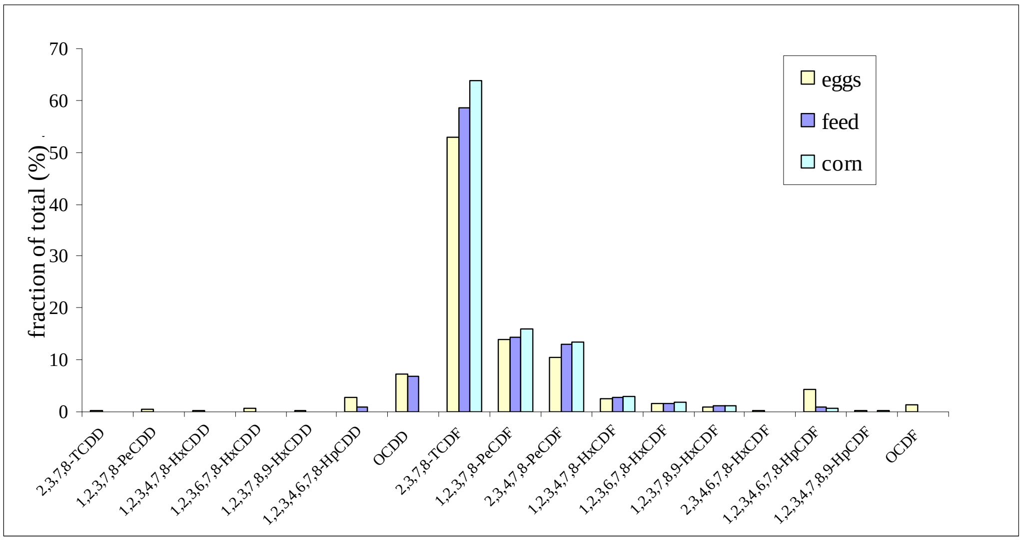

Figure 1. Congener patterns of the highest contaminated eggs, feed (average of 3 samples) and corn (average of 6 samples), expressed as fraction of the absolute levels.

In fact, the current EU-limit for feed is much too high to guarantee that the eggs will remain below the limit. Furthermore, the low chlorinated furan congeners in the feed previously showed an excellent carry-over to eggs.
The feed company subsequently send samples of all the ingredients used in the contaminated feed to a private laboratory. This resulted in the disclosure of the source, being organic corn imported from the Ukraine. The sample showed a level just above the maximum limit of 0.75 ng TEQ/kg. RIKILT also received 6 samples of this corn and obtained dioxin levels varying between 2.03 and 2.65 ng TEQ/kg with an average of 2.40 ng TEQ/kg. With feed containing 30-40% of this corn, the previously observed feed levels could be explained. Again, the pattern was identical with that in the feed and the eggs, showing the dominance of TCDF, the two PeCDFs and minor amounts of PCBs (Figure 1). The level of indicator PCBs was low, being 1.12 µg/kg. The ratio between the 6 indicator PCBs and the dioxin TEQ level thus was around 500.

Source of the contamination
Although the vitamin A seemed initially a potential source of the contamination, this became unlikely once the corn was shown to be the real source. The question is therefore how the corn could have become contaminated. A remarkable observation is the rather low variation in the levels in the corn, rendering a point source as very unlikely. Therefore another potential explanation is the drying process and the use of contaminated fuel, very similar to the situation around the contaminated bread crumbs in Ireland in 2008. Although the relative amounts of PCBs in the corn were very low, and also the ratio between PCBs and dioxins, this situation does not differ very much from that in Ireland, where PCB-oil in the fuel was identified as the source. Actually, the ratio in Irish bread crumbs analysed at RIKILT was only 166, being even lower than that in the corn. Also the contribution of dioxin-like PCBs to the TEQ level was very low in both incidents. However, the furan pattern in the present case is clearly different with a dominance of the TCDF whereas in the Irish case one of the PeCDFs also contributed strongly (Figure 2A). For comparison, also the Belgian feed is included showing a clear dominance of the higher chlorinated furans. However, in that incident the oil was not burned. When focusing on the dioxin-like and indicator PCBs there appears to be a shift in the current incident towards the lower chlorinated ones with PCB 118 being the most dominant and virtually no PCB 180 (Figure 2B). Also PCB 28 was quite abundant in comparison with the Irish and Belgium incidents.

The corn came from a shipment of 2500 tons, imported from the Ukraine and delivered to various feed companies. Examination of other batches also showed levels around 1 ng TEQ/kg. Assuming an average level around 2 ng TEQ/kg the total amount of dioxin TEQ in the shipment would be 5 mg TEQ. The total amount of PCBs was estimated to be around 2-10 g.

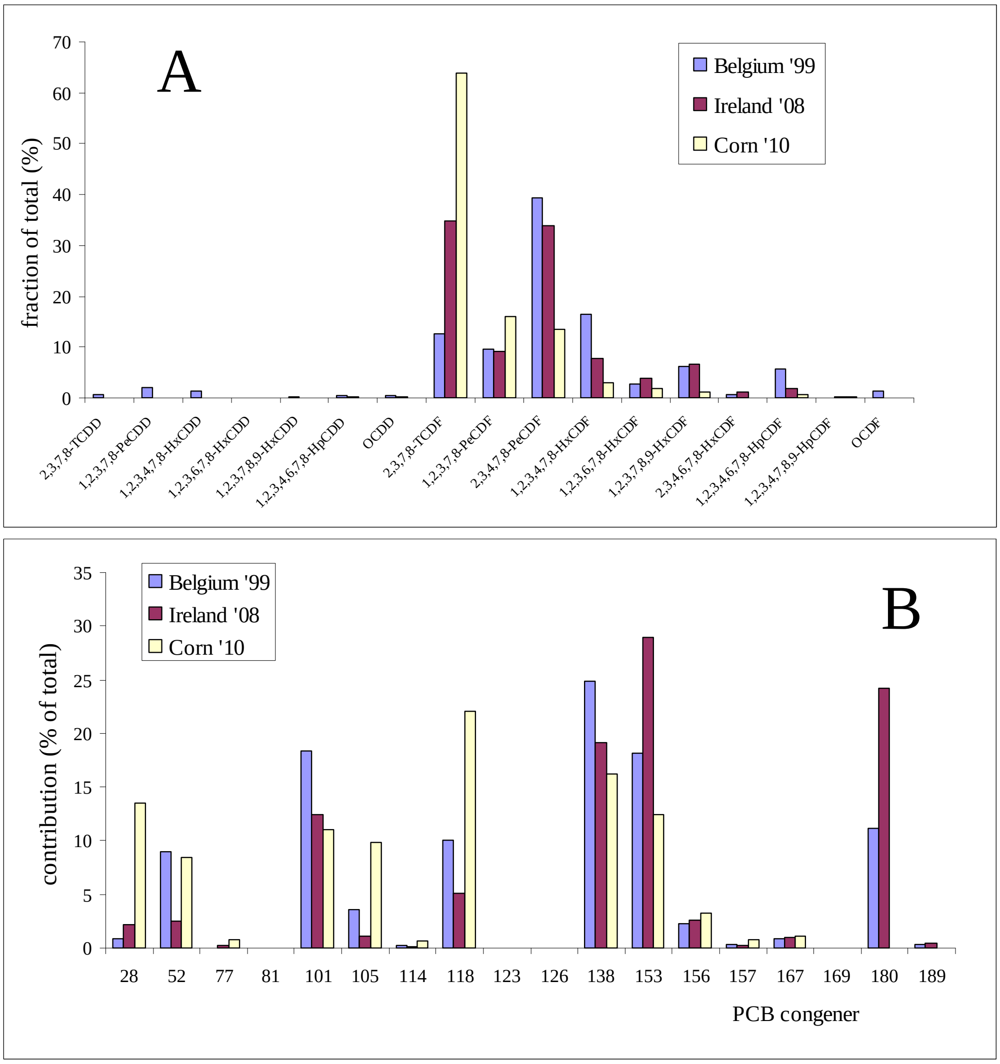

Figure 2. Comparison of PCDD/F (A) and PCB (B) congener patterns of the current incident with corn with 2 PCB-related incidents (5,6).

Application of the DR CALUX assay

The first contaminated egg was picked up with the bioassay, showing a clearly elevated response. Follow-up actions involved confirmation by GC/HRMS and for RIKILT examination of very few samples, already highly suspected samples, all covered by GC/HRMS. The feed samples analysed by GC/HRMS were also tested in the DR CALUX assay and showed a clearly elevated response. Actually, the indicative levels were 3-4 fold higher in the bioassay, suggesting the presence of other compounds in the contaminated feed that might have a response in the test. This could be e.g. other non-2,3,7,8-substituted PCDD/Fs which are far less resistant to degradation and as such might not accumulate in the body.

Once the number of potentially contaminated farms increased, the bioassay was again used to test egg samples in order to increase the capacity. Since in principle GC/MS can produce test results within 2 days for a limited amount of samples, some samples were also checked by GC/HRMS as long as the bioassay did not produce results. This allowed a comparison of DR CALUX and GC/HRMS and a better tuning of the bioassay based on these samples. It was e.g. shown that the congener pattern in the eggs would result in a slight overestimation of the level by the bioassay and that as such the cut-off level could be slightly increased.

Consequences of the incident

The relatively low contamination was initially not detected by the producer of the corn or the feed. It showed up because it caused elevated levels in eggs of laying hens that received the feed for a substantial amount of time, causing the gradual increase in the egg levels. This draws again the attention to the fact that the feed limits for laying hens are too high to guarantee eggs below the maximum limit. One might argue that that the corn was clearly over the limit and should as such not have been used in the feed. However, some of the levels detected in the corn were only slightly over the limit, especially when taking into account the measurement uncertainty of the method applied. Nevertheless, feed may be produced from such corn that may eventually cause levels in eggs that exceed the action limit for dioxins.

This also draws the attention to the analytical procedures used for the analysis. During the incident, it was observed that low resolution GC/MS had been used for analysis of feed and food samples, possibly resulting in false-negative results. This method is currently not accepted as a confirmatory method for dioxins and dl-PCBs in the EU but can be regarded as a screening method. However, in that case it should use cut-off levels well below the maximum levels in order to avoid a too high fraction of false-negative results. Such a method might certainly be able to detect strongly increased levels but is apparently not fit to detect levels around the maximum or action levels, which may nevertheless result in a food incident with large consequences for the farmers and feed companies.

Another interesting issue is the fact that the focus in the food chain is still very much on the dioxins and much less on the dioxin-like PCBs. Actions are taken on eggs that do exceed the limit for dioxins but not the limit for the sum of dioxins and dioxin-like PCBs. The question is whether this is a sound situation. Also analytical reports often include only the dioxins and suggest that the food producers do not ask for the analysis of dioxin-like PCBs.

Prolonged feeding of contaminated feed will not only result in elevated levels in the eggs but also in the body fat of the hens. Following the switch to clean feed, the levels in the eggs will initially show a sharp drop since the major source is gone. However, the body fat will subsequently become the most important source of the dioxins in the eggs and as a result cause the contamination of eggs during a prolonged period. This elimination process is rather slow and it was calculated that during this period it takes about two months to decrease the levels from around 6 pg TEQ/g fat to below the maximum level of 3 pg TEQ/g fat.

Last but not least is the question whether the current incident might present a potential risk for the consumer. Daily consumption of eggs contaminated at 10 pg TEQ/g fat would result in a weekly exposure of 420 pg TEQ based on 6 grams of fat per egg. On a body weight base this would be 6.5 pg TEQ/kg bw/week which would correspond to 46% of the Tolerable Weekly Intake (TWI) and probably result in an overall exposure of most consumers around the TWI. As such, this would not result in an increased health risk, especially when only temporarily. However, the intention behind the actions on dioxins is to decrease the exposure of consumers to levels well below the TWI and as such this situation is far from desirable.

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