Kaolinic clay derived dioxins in potato by-products

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Introduction

The current exposure of at least part of the European population to dioxins and dioxin-like compounds still exceeds the exposure limit of 14 pg TEQ/kg bw/day. Therefore, strategies for further reduction aim at the identification of sources of these compounds and their entry points into the food chain. This is achieved by a set of maximum limits and action limits, combined with monitoring programs on feed and food. Last year this resulted in the identification of the use of contaminated kaolinic clay for sorting out poor quality potatoes. Since potato by-products were used as animal feed, this caused a elevation of dioxin levels in milk and fat. The current paper describes the discovery of the incident, the magnitude and consequences, and the elimination kinetics in milk at the highest contaminated farm.

Materials and Methods

HRGC/HRMS analysis

HRGC/HRMS analysis was performed as described previously by Tuinstra et al.[1] In short, samples were fortified with ^{13}C-labelled standards and subsequently purified on a gel-permeation, an aluminium oxide and an activated carbon column. The two fractions eluting from the last column were analysed for respectively the dioxins and non-ortho PCBs, and the mono-ortho PCBs.

CALUX-analysis

CALUX analysis was performed as described previously. In short, 5 gram of product was suspended in 15 ml methanol/water 85/15 (v/v) and extracted with hexane/diethyl ether 97/3 (v/v). The extract was cleaned over a 33% acid silica column (10 g). Fat (0.5 g) was mixed with hexane/diethyl ether and directly applied to the acid silica columns. The eluate was dried to a small volume, mixed with 40 µl DMSO and further dried to remove the organic solvent. The DMSO was mixed with culture medium, which was then added to the cells. After a 24 h incubation period cells were lysed and the luciferase measured using an Ascent luminometer (Thermo Labsystems). The response was compared to that of a set of chicken feed samples containing 0, 0.3, 0.6, 0.8, 1.8 and 3.8 ng TEQ/kg of a mixture of dioxins and dioxin-like PCBs. Samples showing a higher response than the sample of 0.6 ng TEQ/kg were declared "suspicious" and analysed by GC/MS. In the case of fat a natural contaminated milk fat sample containing 0.5 ng TEQ/kg and the same fat enriched to levels of 1, 2, 3 and 6 ng TEQ/kg was included in each series, as well as a carbon cleaned fat sample. Samples were declared "suspicious" if the response was higher than the sample containing 2 ng TEQ/kg.

PBPK-model analysis

A physiologically based pharmacokinetic (PBPK) model derived from a model presented by Derks *et al.*[2] was employed to analyse the kinetics of milk contamination and to predict the decontamination after cessation of feeding the contaminated potato peelings. Three samples in milk served model calibration with respect to the start of feeding the contaminated peels and the fraction that is absorbed from the peelings over the gut wall.

Results and Discussion

Discovery of the incident

In august 2004 a pooled milk sample, analysed as part of a monitoring project on milk in the Netherlands, was shown to contain an elevated level of dioxins. The sample contained a level of 1.5 pg TEQ/g fat as compared to background levels around 0.5 pg TEQ/g fat. The sample was composed of milk from three different milk collection trucks. Screening of the individual collections by CALUX revealed one elevated sample which was subsequently analysed by GC/HRMS and shown to contain 5 pg TEQ/g fat. The three farms that delivered their milk to this truck were visited and sampled. The milk was screened by CALUX and again showed one elevated sample. The GC/HRMS result showed a total TEQ-level of 20 pg TEQ/g fat, primarily derived from dioxins.

Source identification

The congener pattern in the milk was compared to that of other known sources and resembled that of contaminated kaolinic clay analysed in the summer of 1999 (Figure 1), especially when taking into account the carry-over rates for the different congeners from feed to milk[3]. There was a high contribution to the total TEQ level from TCDD and PeCDD. The relatively poor carry-over of higher chlorinated dioxins explained the slight changes in the pattern, like the low levels of the hexa and in particular the hepta and octa congeners.

The inspection service of the VWA visited the farm and was asked to look specifically for this material, however without success. All feed items were collected and screened with CALUX, revealing that in particular potato peels showed a clearly elevated response, high enough to account for the elevated milk levels. Some other feed items had apparently been cross-contaminated with this material. GC/HRMS analysis confirmed the screening result and showed a pattern similar to the milk. The potato peels were by-products from the wastewater treatment plant of a Dutch producer of French fries and other potato products. Levels amounted to 44 ng TEQ/kg (88% dw). The farmer in question was one of the few to obtain this wet material that was fed to the cows at a ration of 20 kg/day ww or about 2 kg/day dw. Initially it was unclear how the potato peels were contaminated but eventually it became evident that the company recently changed its procedure for sorting out low density potatoes. Initially a salt bath was used for this purpose but for environmental reasons the producer had switched to a bath with different types of clay, including kaolinic clay. Analysis of a number of clay samples revealed levels around 1 to 2 µg TEQ/kg with a pattern very similar to that in potato peels (Figure 1, kaolinite 2004).

Size of the incident

The production process of the company was carefully analysed in order to identify other products that could have been contaminated. In addition to the potato peels used by the contaminated farm, several other waste products are produced during the production including grey starch from the waste water plant, poor quality potatoes from the sorting process, steamed peels and badly sized potato cuts. The starch used for covering stored grass and other fodders was shown to be contaminated at levels up to 30 ng TEQ/kg. This could be explained by the fact that it was also a by-product from the waste water facility and as such was contaminated with the clay. However, only small amounts of this material may have been fed to the animals. The peels derived from the steaming process were also contaminated with maximum levels up to 15 ng TEQ/kd (88% dw). However, in practice this material is first collected and cooked, and during this process mixed with non-contaminated material before being fed to pigs. This may explain the fact that no elevated dioxin levels were found in pig fat samples at farms feeding the product thus obtained. The poor quality potatoes did not show levels above the action, but in this case the peel only represents a small part of the product. Similarly, the potato cuts, but also French fries for human consumption were negative, which is in line with the fact that the potatoes and fries are cut after peeling and washing.

Overall, although hundreds of farms were blocked as a precaution, only three milk farms showed clearly elevated dioxin levels.

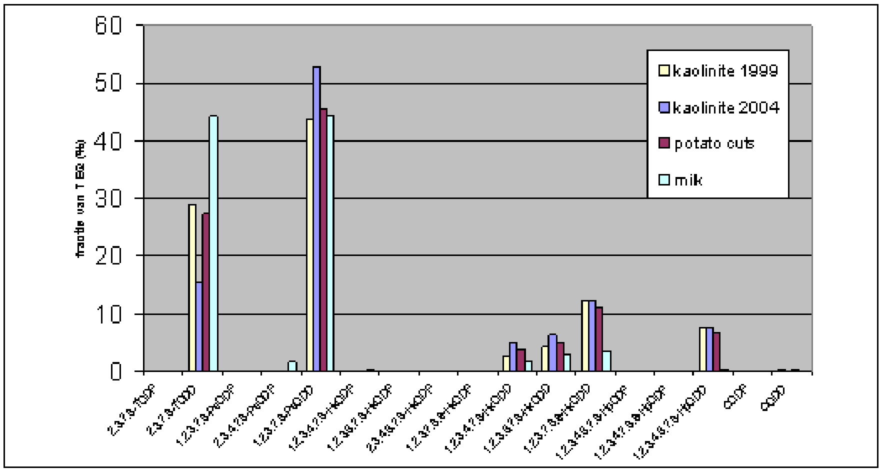

Figure 1. Congener pattern, expressed as relative contribution to the TEQ level, for the contaminated milk sample as well as the potato peels, the kaolinic clay employed in the potato sorting bath (2004), and a kaolinic clay sample from 1999.

Depletion of dioxins in milk

Milk from the most contaminated farm was regularly sampled and analysed by GC/HRMS. Cows at this farm received up to 20 kg of the wet potato peels per day, amounting to a daily exposure of about 90 ng TEQ/day. Using carry-over rates for feed to milk of around 0.3 or lower[3] and a daily milk fat production of 1 kg, it can be calculated that at steady state maximum milk levels would be around 20-25 pg TEQ/g fat. This was corroborated by PBPK model analysis. Levels are shown in Figure 2, including the level estimated from the first sample. The corresponding calculated steady-state level after about 150 days is 23 pg TEQ/g fat, and the carry-over rate for total TEQ 0.26. In agreement with previous studies[4], after start and cessation of feeding the contaminated peels, there was a rapid first rise/decline, followed by a much slower one. The calculated half-life for the first period was about 1 day, the half-life for the slow elimination phase was about 4 weeks. In practice, levels decreased 50% during the first week and than required two months to decrease to the residue limit of 3 pg TEQ/g fat.

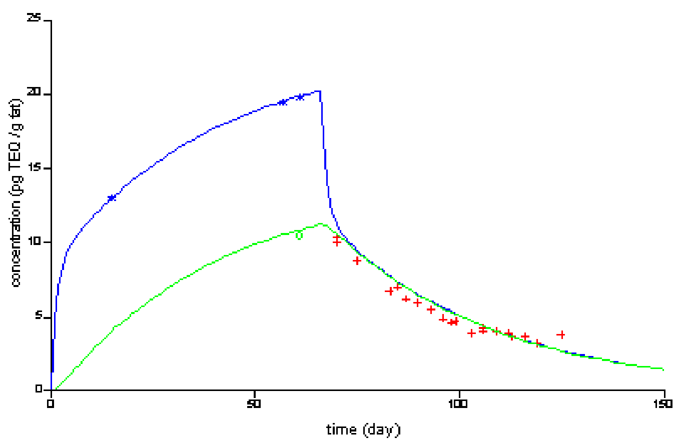

Figure 2. A standard PBPK model describing the kinetics of dioxin in the cow was calibrated on three concentration in milk data during the phase of contamination (*) by fitting the starting day of feeding contaminated peelings. The model was used to calculate levels in milk fat (upper line) and body fat (lower line) and compared to data in milk fat (+) taken after cessation of the contamination and one body fat sample (o).

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