BUFFALO MILK PROCESSING: TRANFER OF PCDD, PCDF, AND DL-PCB CONGENERS TO MOZZARELLA, WHEY, AND WHEY CHEESE

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Introduction

Buffalo milk is almost completely delivered to cheese plants to produce mozzarella, a typical Italian cheese of protected geographical origin. The high fat content (9 %) of the milk, and the hydrophobicity of casein protein precipitates during milk processing, prompted us to study the transfer of polychlorodibenzodioxins (PCDDs), polychlorodibenzofurans (PCDFs), and dioxin-like polychlorobiphenyls (DL-PCBs) from raw buffalo milk to its dairy products (mozzarella, whey, whey cheese). The aim was to assess if any changes following processing occurred in TEQ contamination levels and in the analytical congener profiles of PCDDs, PCDFs, and DL-PCBs. The outcome could be of interest to predict mozzarella compliance with regulatory levels based on occurrence data of raw milk. Moreover, provided the fat content and consumption of cheese were known, it could be envisaged to use a cheese contamination value estimated from raw buffalo milk data for intake assessment.

Materials and methods

During the Italian buffalo milk "dioxin" crisis in 2008 [1], it was possible to trace back exposed buffalo herds and draw contaminated bulk milk from three different farms (A, B, C). The three bulk milks were then processed in a dedicated small scale cheese plant, according to the following procedure. In brief, bulk milk temperature was brought to 38.8–39.0 °C and, after addition of liquid rennet (title 1:15,000), the coagulation took place in 10–12 min. The curd was cut with a knife into four segments 60 min later, and to hazelnut-like pieces after additional 30 min. Then, 70 % of the whey was removed and the curd was allowed to ripen soaked in the remaining whey for 90–120 min, until a pH value of 5.10–5.05 was reached. After the addition of boiling water, the curd was stretched with a wooden stick into a smooth, plastic mass, manually molded into balls weighing approximately 100 g each. They were cooled in water at 8–12 °C for some 20 min and then stored at 6 °C in a brine containing 3 % NaCl (w/v), thus obtaining mozzarella as a final product. Whey cheese was recovered after boiling the whey, and collected into plastic sieves. An exhaustive lipid extraction from selected matrices was performed with a mixture of methanol, diethyl ether, and *n*-hexane (1:1:1, v/v). Analysis of PCDD, PCDF, and DL-PCB congeners was carried out by GC-HRMS [2]. Cumulative TEQ results (2005 WHO TEFs) were expressed on the fat basis as upper bound (UB) values [3]: however, lower and upper bound estimates were always well within 20 % of each other.

Results and discussion

Mozzarella yields from buffalo milk were 19 ,16, and 27 % for farms A, B, and C, respectively, on a gravimetric basis.

Figure 1 shows the cumulative levels (WHO TEQ) found in buffalo milk and its dairy products from farms A, B, and C. Figure 2 allows a comparison of contamination profiles in milk and mozzarella, normalized on the most abundant congener and grouped by PCDDs+PCDFs, non-*ortho* DL-PCBs, and mono-*ortho* PCBs.

The cumulative levels found in raw milk from farms A, B, and C were greater by a factor of 4 (farms A and C) and a factor of 6 (farm B) than the current EU legislative limit of 5.5 pgTEQ/g fat in dairy products, thus representing well some specific situations monitored during 2008 in field conditions. From Figure 1, it is evident that mozzarella cheese was always more contaminated than the corresponding raw milk used to produce it: this is true even when PCDD+PCDF and DL-PCB contributions to total TEQ values are considered separately. The differences observed between farms A, B, and C in contamination transfer rates may be attributed to a different quality of the milk relative to its inherent protein content (see mozzarella yields above): casein proteins precipitate during milk processing due to their increased hydrophobicity after the cleavage of the phospholipidic moieties by the liquid rennet. In small scale cheese plants, such as those usually processing buffalo milk, the aforesaid variations may occur from batch to batch as, indeed, it is the cheese-maker's skill the key factor in determining mozzarella quality and yield. Changes in milk quality may also happen according to a different animal husbandry at farm and the seasonal variations in forage supply. Conservatively, a cumulative TEQ increase in mozzarella of up to 30 % relative to the contamination level recorded in raw milk (farm C, Figure 1) cannot be excluded. Due to the low protein content in whey, whey cheese could not be recovered in farm C.

The congeners profiles shown in Figure 2 do not highlight any appreciable modifications in contamination patterns between milk and mozzarella. This suggests that protein precipitates do not exert any selection on congener co-precipitation despite the differences in K_{OW} magnitude for PCDD, PCDF, and DL-PCB congeners, greater than a factor of 10.

The analytical profiles found in milk (Figure 2) are well representative of those congeners most contributing to TEQ values and may also allow transferring our findings to other PCDD, PCDF, and DL-PCB contamination scenarios in buffalo dairy products. As to intake assessment, in the case of a lack of specific occurrence data on buffalo cheese, it could be feasible to use the appropriate conversion factors to conservatively extrapolate the contamination found in fresh milk to the cheese. We propose the described experimental approach also for dairy products from species other than buffalo, that may recognize a different composition of the milk with respect to fat and proteins, and a different processing for cheese production.

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References

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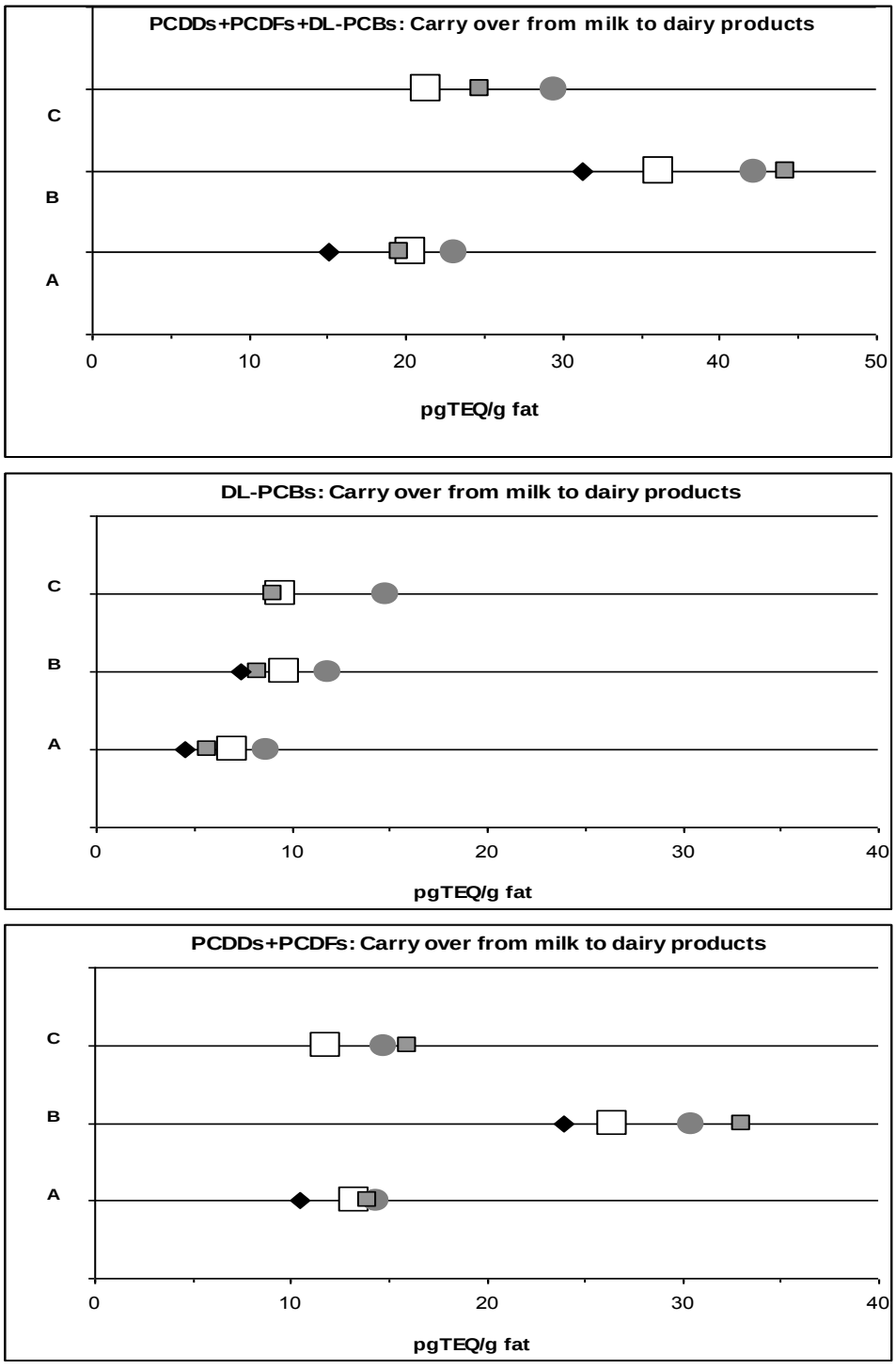

Figure 1. Cumulative PCDD+PCDF and DL-PCB levels (2005 WHO TEQ values, upper bound) in contaminated raw buffalo milk samples from farms A, B, and C, and in the derived dairy products. Raw milk □; mozzarella ●; whey ■; whey cheese ♦.

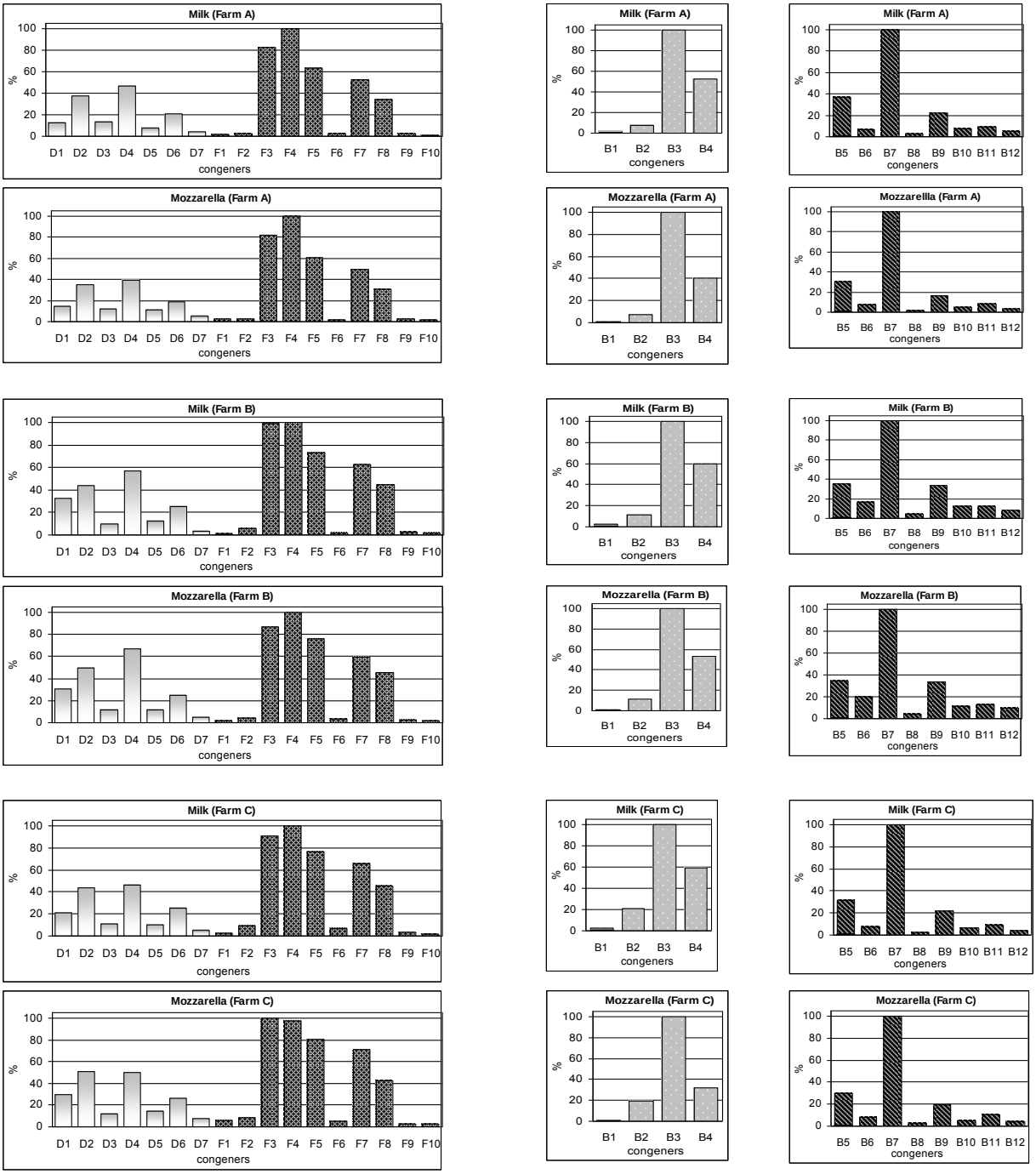

Figure 2. PCDD+PCDF (left), non-*ortho* PCB (middle), and mono-*ortho* PCB (right) congener profiles in buffalo milk and in the corresponding mozzarella from farms A (top), B (middle), and C (bottom).

Legend: D1, 2,3,7,8-T_4CDD; D2, 1,2,3,7,8-P_5CDD; D3, 1,2,3,4,7,8-H_6CDD; D4, 1,2,3,6,7,8-H_6CDD; D5, 1,2,3,7,8,9-H_6CDD; D6, 1,2,3,4,6,7,8-H_7CDD; D7, O_8CDD; F1, 2,3,7,8-T_4CDF; F2, 1,2,3,7,8-P_5CDF; F3, 2,3,4,7,8-P_5CDF; F4, 1,2,3,4,7,8-H_6CDF; F5, 1,2,3,6,7,8-H_6CDF; F6, 1,2,3,7,8,9-H_6CDF; F7, 2,3,4,6,7,8-H_6CDF; F8, 1,2,3,4,6,7,8-H_7CDF; F9, 1,2,3,4,7,8,9-H_7CDF; F10, O_8CDF; B1, PCB-77; B2, PCB-81; B3, PCB-126; B4, PCB-169; B5, PCB-105; B6, PCB-114; B7, PCB-118; B8, PCB-123; B9, PCB-156; B10, PCB-157; B11, PCB-167; B12, PCB-189.