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Levels of PCDDs, PCDFs and dioxin-like PCBs in raw cow's milk collected in France in 2006

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Abstract

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) as well as polychlorinated biphenyls (PCBs) are widespread environmental contaminants. A French national survey was carried out in April 2006 to assess the concentrations of PCDD/Fs and dioxin-like PCBs (DL-PCBs) in raw cow's milk. A random sampling scheme stratified by region was applied to collect 239 raw milk samples from 93 plants belonging to 17 dairy companies. Compared to a previous survey led in 1998 analyzing half-skimmed drinking milk in France, the PCDD/Fs level was cut by half, with an average concentration of 0.33 pg toxic equivalent (TEQ)/g fat in 2006. The mean DL-PCBs concentration was 0.57 pg TEQ/g fat and subsequently the sum of PCDD/Fs and DL-PCBs was 0.90 pg/g fat, values below the thresholds defined by the European Union regulations.

Keywords: Dioxin; Milk; PCDD; PCDF; PCB; France

1. Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), collectively termed dioxins, as well as polychlorinated biphenyls (PCBs) are widespread environmental contaminants. Because of their lipophilicity and their low biodegradability, PCDD/Fs and dioxin-like PCBs (DL-PCBs) tend to accumulate in the food chain. Grazing cows ingest contaminated grass and these contaminants are rapidly absorbed from the gastrointestinal tract. They accumulate in the liver and adipose tissues including the milk fat of the lactating cows, which is the main excretion pathway for these contaminants (Fürst et al., 1993; Schuler et al., 1997).

In human, toxicity of dioxins is related to the amount accumulated in the body during lifetime. The acute health effects in people exposed to large amounts of dioxins are dermal effects such as chloracne. Other main concerns are the risk of cancer and, based on animal studies, reproductive or developmental effects (Kogevinas, 2001).

European Union (EU) regulation no. 199/2006 on food safety establishes maximum levels for a number of contaminants in foodstuffs including PCDD/Fs (Table 1), expressed in World Health Organisation (WHO) toxic equivalents (TEQ) using the WHO-TEF (toxic equivalency factors established in 1997). For consumer's health protection, when placed on the market, milk and dairy products must not contain PCDD/Fs levels higher than 3 pg TEQ/g fat. In order to actively reduce the presence of dioxins in foodstuffs, this threshold is accompanied by measures stimulating a proactive approach such as the use of action levels: tools for competent authorities and operators to

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Table 1
Maximum limits and action levels for PCDD/Fs and dioxin-like PCBs in milk and milk products

Commission Regulation (EC) no. 199/2006 of 3 February 2006		Commission Recommendation of 6 February 2006 (2006/88/EC)	
Maximum levels (pg TEQ/g fat)		Action levels (pg TEQ/g fat)	
PCDD/Fs	PCDD/Fs+DL-PCBs	PCDD/Fs	DL-PCBs
3	6	2	2

identify a source of contamination and to take measures for its reduction or elimination. The action threshold for PCDD/Fs in milk and dairy products is 2 pg TEQ/g fat (Recommendation, 2006/88/EC). Moreover, a maximum concentration of 6 pg TEQ/g fat has been defined for the sum of PCDD/Fs and DL-PCBs and the action level is 2 pg TEQ/g fat for milk and dairy products for DL-PCBs.

In France, the levels of PCDD/Fs were first quantified in 1998 in half-skimmed drinking milk through a national survey in which a mean of 0.65 pg TEQ/g fat was found. This value was significantly lower than the maximum level allowed by the regulation at this period (5 pg TEQ/g fat) (Durand et al., 2000). Since 1998, measures were initiated by French government to reduce the release of dioxins into the environment, and it was thus interesting to follow the milk contamination level. The National Interprofessional Center for the Dairy Economy sponsored a survey during Spring 2006 to draft an overall picture of the contamination of raw cow's milk by dioxins and PCBs. The study design is intended for two purposes. A first level purpose is to estimate the PCDD/Fs and DL-PCBs contamination levels of the raw cow's milk at the national level. The second level purpose is source directed and leads to evaluate the spatial variations of the contaminations at the regional level.

2. Materials and methods

2.1. Sampling

A total of 17 dairy groups processing raw cow's milk in France accepted to participate to the study. They correspond to 115 plants, spread over 20 of the 22 French regions. The sampling base was thus the raw milk collected by these 115 plants: 11×10^9 milk liters in 2005. This corresponds to half of the national milk collection, estimated to 22×10^9 l for 2005.

For each of the 20 regions, the volume of raw milk collected yearly was computed using data obtained from the dairy groups, at the plant level. The resulting figures varied widely. In order to obtain satisfactory precision of the estimates both at the regional and at the national level, the global number of 250 samples was stratified by region as follows:

- 5 samples were allocated to each of 4 regions having collected less than 100×10^6 litres in 2005;
- 10 samples were allocated to each of 16 regions having collected more than 100×10^6 litres in 2005;
- the remaining 70 samples were also allocated to the preceding 16 regions, in proportion to the 2005 collection.

Finally, within each region, the samples were randomly allocated to the dairy plants, the draw probability being proportional to the milk amount collected by the plant in 2005. Out of 115 plants, 93 were eventually included in the sampling protocol. The number of samples *per* plant varied from 1 to 6 samples.

In each plant, samples were collected from bulk tanks over a 2 weeks period (April 2006). A standardized procedure was defined so that samples were taken from different rounds, combining several areas and dates of collection. Samples were aliquoted in 2 l polyethylene bottles and stored between −18 °C and −30 °C before sending the containers to the laboratory for analysis, accompanied by a monitoring sheet.

2.2. Analytical procedures

Analyses were carried out in an accredited laboratory. Seventeen PCDD/Fs congeners and 12 DL-PCBs (PCB 81, PCB 77, PCB 126, PCB 169, PCB 123, PCB 118, PCB 114, PCB 105, PCB 167, PCB 156, PCB 157 and PCB 189) were measured using gas chromatography coupled with high resolution mass spectrometry. Milk samples were extracted according to the method described by Liem et al. (1990). Three hundred and fifty gram of milk was fortified with a standard mixture of $^{13}C_{12}$-labelled PCDD/Fs (500 pg for tetra to heptaCDD/Fs, 1000 pg for OCDD and OCDF) and $^{13}C_{12}$-labelled PCBs (1000 pg for mono and non-ortho PCBs, 5 ng for di-orthoPCBs). Sodium oxalate and methanol were added and the fat fraction containing PCDD/Fs and PCBs was extracted by liquid–liquid extraction using diethyl ether and petroleum ether. Combined ether fraction was dried over sodium sulphate and evaporated to dryness. The fat amount was determined at constant weight. Then, the fat was dissolved in hexane and the fatty co-extracted material was removed by sulfonation.

Organic extract was purified on Power-Prep (Fluid Management System, USA). Briefly, this system uses disposable multi-layer silica column, basic alumina and carbon columns in order to separate analytes of interest from matrix interferences, and allows the operator to collect different fractions at different steps of the purification. Di and mono–ortho PCBs were eluted in the first fraction (elution with hexane and dichloromethane) whereas