LEVELS OF POLYCHLORODIBENZO-DIOXINs (PCDDs) and POLYCHLORODIBENZO-FURANs (PCDFs) IN MILK IN FRANCE

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ABSTRACT

57 cow milk samples collected in 14 different departments in France through the services of the Ministry of Agriculture have been analyzed for PCDDs and PCDFs. The location of the samples has been set with regard to industrial background in each administrative French department: the grazing fields were selected especially in the vicinity of industrial sites (municipal solid waste incineration plants, cement works, chemical industries, etc.).

One of the selected departments had no industrial activity.

Moreover, 46 cow milk samples have been collected in some of the same locations but at different seasons of the year to evaluate seasonal influence.

The average I-TEQ content on milk fat basis amounts to 1.68 pg/g which is much lower than the Standard of 6 pg/g (worldwide accepted limit).

INTRODUCTION

In 1994, the French Ministry of Agriculture set up a survey aimed at assessing the PCDDs and PCDFs content of the cow milk produced in France. This survey is the first survey of the magnitude that has been performed on 14 different administrative departments which are important milk producers in France and based (i) on different locations in each department to take into account industrial background and (ii) on different periods of the year.

PROCEDURE FOR SAMPLING AND ANALYSIS

SAMPLING PROCEDURE

The sampling was performed in July 94 by the local services of the Ministry of Agriculture in each of the 14 selected departments. One of these was selected because of the anticipated absence of contamination and absence of industrial activity. The others were selected especially in the vicinity of Municipal Solid Waste Incineration Plants.

In each of the 14 departments, it was decided to take 5 samples of raw cow milk. Out of these 5 samples, 4 came from 4 different independent dairy farms selected on the basis of industrial site in their vicinity. The fifth was a pooled sample collected from miscellaneous milk tanks in a centralized dairy.

An additional sampling was organized in 4 of the 14 departments with 4 samples per department, 2 from an independent dairy farm and 2 from a centralized dairy (i.e. 48 samplings). These samplings were carried out in October 94, January 95 and April 95 to assess the seasonal variation.

All samples were taken in pre-cleaned brown glass vials, frozen and transported to the analytical laboratory where the samples were stored at -30°C until analysis. Detailed instructions were given to the people in charge of the sampling.

ANALYTICAL PROCEDURE

Analyses of milk samples have been carried out according to the method described by Liem et Al[i]. Shortly, milk samples were fortified with known amounts of sixteen $^{13}C_{12}$-labeled PCDD and PCDF standards. The milk fat fraction was then isolated by a liquid-liquid extraction procedure using organic solvents (diethyl ether and petroleum ether).

The fat fraction was dried and weighed.

The clean-up of the fat fraction, redissolved in dichloromethane was performed by Carbosphere active carbon column chromatography followed by alumina column chromatography. The final purified extract was concentrated in 25 μl of dodecane containing two internal standards ($^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD). A volume of 1.5-2 μl was used for HRGC-HRMS quantification. The resolution of the mass spectrometer was set at 10,000 resolution.

RESULTS

The results of the first sampling from 14 departments milk analyses have been summarized in table 1 as toxicity equivalents. These results show on average of 1.74 pg/g TEQ fat (period of July 94).

Table 1: Summary of the PCDDs and PCDFs content of the 57 samples of cow milk from 14 French departments.

DEPARTMENTS	NUMBER OF SAMPLES	Σ I-TEQ DIOXINS pg/g fat (mean)	Σ I-TEQ FURANS pg/g fat (mean)	Σ I-TEQ TOTAL pg/g fat (mean)
1	4	0,43	0,56	0,99
2	2	0,39	0,45	0,84
3	5	0,40	0,92	1,32
4	5	0,55	0,92	1,47
5	5	0,61	1,83	2,44
6	5	0,34	0,48	0,82
7	5	0,37	0,58	0,95
8	5	0,44	0,87	1,31
9	2	1,36	2,67	4,03
10	5	0,43	0,51	0,94
11	2	0,83	2,12	2,95
12	5	1,78	2,46	4,24
13	5	0,59	1,49	2,08
14	2	0,61	0,69	1,30

Table 2:

Seasonal variations were studied through 4 periods for 4 departments with 46 samples:

- first period: July 94 (see table 1)
- second period: October 94
- third period: January 95
- fourth period: April 95.

The results are shown in table 2: PCDD/Fs contamination levels (on fat basis) of the analyzed milk from the selected departments are slightly lower in winter and spring than in autumn. The levels of autumn are globally slightly lower than those of the first period (summer).

Table 2: Summary of I-TEQ (pg/g fat) in whole milk from four departments

DEPARTMENTS AND PERIODS	NUMBER OF SAMPLES	Σ I-TEQ DIOXINS pg/g fat (mean)	Σ I-TEQ FURANS pg/g fat (mean)	Σ I-TEQ TOTAL pg/g fat (mean)
3				
2nd period	4	0,50	0,53	1,03
3rd period	3	0,51	0,45	0,96
4th period	4	0,31	0,27	0,58
4				
2nd period	4	0,68	0,81	1,49
3rd period	3	0,48	0,61	1,09
4th period	4	0,56	0,70	1,26
8				
2nd period	4	0,60	0,60	1,20
3rd period	4	0,38	0,58	0,96
4th period	4	0,44	0,68	1,12
12				
2nd period	4	1,50	1,80	3,30
3rd period	4	1,39	1,84	3,23
4th period	4	1,18	1,57	2,75

[i] Litterature: Liem A.K.D., De Jong A.P.J.M., Marsuman J.A., De Boer A.C., Groenemeijer G.S., Van der Heeft E., De Korte G.A.L., Hoogerbrugg R., Den Hartag R.S., Kootstra P.R., Van't Klooster H.A., Chemosphere, 20, 7-9, 843-850, 1990a.