

ANALYSIS OF POLYCHLORODIBENZO-DIOXINS (PCDDs) AND POLYCHLORODIBENZO-FURANS (PCDFs) IN MILK AROUND INDUSTRIAL SITES IN FRANCE

S. Defour⁽¹⁾, D. Fraisse⁽¹⁾, M.C. Scherrer⁽¹⁾, B. Schnepf⁽¹⁾, F. Le Querrec⁽²⁾

⁽¹⁾ CARSO, 321 avenue Jean Jaurès F-69362 LYON CEDEX 07

⁽²⁾ Ministry of Agriculture and Fisheries - Directorate General for Food
251, rue de Vaugirard - 75015 PARIS

ABSTRACT

On March 17, 1998 the CSHPF (French Superior Counsel of Public Health) issued a statement specifying the following guidance limits for PCDDs and PCDFs concentrations in milk :

- 5 pg I-TEQ/g fat is the limit for trade of milk and dairy products,
- 3 pg I-TEQ/g fat is the value which generates a search of PCDD/PCDF sources and steps to rapidly reduce these sources,
- < 1 pg I-TEQ/g fat : target to be met for all milk and dairy products of large consumption.

In this respect, the Ministry of Agriculture and Fisheries launched a survey to assess the concentration of PCDDs and PCDFs in 49 cow milk samples from farms around 26 industrial sites chosen for their potential high level of pollution.

The samples were collected in the last quarter of 1997 and analysed for PCDDs and PCDFs.

- 46 samples are under 3 pg I-TEQ/g fat with an average of 1.53 pg/g I-TEQ fat,
- 1 sample is between 5 and 3 pg I-TEQ/g fat,
- 2 samples are above 5 pg I-TEQ/g fat.

INTRODUCTION

In 1997, the French Ministry of Agriculture and Fisheries decided to add, to the survey carried out in 1994¹⁾ and 1996²⁾ related to PCDDs and PCDFs concentrations in milk and dairy products, the assessment of the PCDDs and PCDFs concentration in cow milk from specific farms around 26 industrial sites chosen for their potential high level of pollution.

EXPERIMENTAL METHOD : PROCEDURE FOR SAMPLING AND ANALYSIS

Sampling procedure

The sampling was performed by the local services of the Ministry of Agriculture and Fisheries around 26 industrial sites.

The industrial sites were related to :

- steel industries,
- secondary lead smelting,
- secondary aluminium smelting,
- copper refining,
- chemical industries,
- oil refinery industries,
- electricity production,
- municipal waste incinerators.

The milk was sampled from farms mainly located at less than 5 km and in no case at more than 11 km under the dominant winds of the industrial site.

The samples were frozen and transported to the analytical laboratory where the samples were stored at - 20° C until analysis.

Analytical procedure

Analyses of samples were carried out according to the method described by Liem et Al.²⁾ Shortly, samples were fortified with known amounts of sixteen ¹³C₁₂-labelled PCDD and PCDF standards. The fat fraction was then extracted by the appropriate method using organic solvents (diethyl ether, petroleum ether...).

Fat content 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 ($^{13}\text{C}_{12,1,2,3,4}\text{-TCDD}$ and $^{13}\text{C}_{12,1,2,3,7,8,9}\text{-HxCDD}$). A volume of 1.5 µl was injected for HRGC-HRMS quantification. The resolution of the mass spectrometer (Ultima-Micromass) was set at 10,000 resolution.

RESULTS

On March 17, 1998 the CSHPF (French Superior Counsel of Public Health) issued a statement specifying the following guidance limits for PCDDs and PCDFs concentrations in milk :

- 5 pg I-TEQ/g fat is the limit for trade of milk and dairy products,
- 3 pg I-TEQ/g fat is the value which generates a search of PCDD/PCDF sources and steps to rapidly reduce these sources,
- < 1 pg I-TEQ/g fat : target to be met for all milks and dairy products of large consumption.

With this statement in view, the results are the following :

- 46 samples are under 5 pg I-TEQ/g fat, with an average of 1.53 pg I-TEQ/g fat,
- 1 milk sample is between 5 and 3 pg I-TEQ/g fat and comes from milk around a chemical industry. This plant will take steps to reduce pollutants in its emissions.
- 2 milk samples are above 5 pg I-TEQ/g fat and come from farms situated at 250 meters and 1 km under the dominant winds of one incinerator in North of France. Because of these results, the local authorities decided to close down this incinerator in February 98 and to ban trade on contaminated milk around the incinerator until the PCDDs and PCDFs concentration in milk decreases under 5 pg I-TEQ/g fat.

It must be kept in mind that these results come from milk produced close to industrial sites (and under dominant winds). In no case, these results can be considered as an average of the concentration of PCDDs and PCDFs in the French milk production. The average concentration in milk and dairy products in France was assessed through the 1996 survey of the Ministry of Agriculture and Fisheries which showed an average I-TEQ content on milk fat basis of 1.33 pg I-TEQ/g fat (52 samples).

LITERATURE CITED

- ¹⁾ D. Fraisse, B. Schnepf, C. Mort-Bontemps, F. Le Querrec (1996)
16th Symposium on Chlorinated Dioxins and Related Compounds - Amsterdam, August 12-16, 1996
Transport & Fate - Environmental Levels - Toxaphenes, PCB's and other Non-Dioxins - Volume 28, 209-212
Levels of polychlorodibenzo-dioxins (PCDDs) and polychlorodibenzo-furans (PCDFs) in milk in France,
- ²⁾ Fraisse, M.C. Scherrer, B. Schnepf, S. Defour, F. Le Querrec (1997)
17th Symposium on Chlorinated Dioxins and Related Compounds - Indianapolis, August 25-29, 1997
Levels in the Environment - Levels in Food - Sources - Volume 32, 283-285
Analysis of polychlorodibenzo-dioxins (PCDDs) and polychlorodibenzo-furans (PCDFs) in dairy products in France,
- ³⁾ 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