STUDY OF THE VARIATION IN PCDD AND PCDF LEVELS IN MILK FROM COWS EXPOSED TO DIFFERENT INCINERATION PLANTS IN DIFFERENT PERIODS

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Introduction

In order to better understand the dynamic of Persistent Organic Pollutants (POPs), models predicting their behavior are made, but it is a great deal to compare and to validate this models with real situations. After 15 years of a great research effort most of dioxin sources are well identified and characterized even thought some new sources are being discovered. Then this knowledge would allow or facilitate to understand the pollution pathways in some natural environments. In fact several studies have been conducted in agricultural food chains.

It is important to understand how these contaminants reach grazing animals, so that the factors controlling the dynamics of their behaviour in the animals can be understood. Many of these studies have used methods under controlled conditions to introduce compounds into the diet of the animal and do not use "naturally contaminated" areas.

This study constitutes part of a more extended research study focused on the study of the influence of two Waste Incinerators in their surroundings, choosing as study element an agricultural food chain, consisting of cows grazing in the vicinity of a Clinical Waste Incinerator (CWI) closed in 1995 and then possibly affected by a new Municipal Solid Waste Incinerator (MSWI) which started operating in 1995.

Cow's milk was chosen because milk is relatively easy to analyse for dioxins and cows graze relatively large areas and any dioxins present on herbage and soil eaten by the cows would concentrate in the fat content of the milk produced. (1).

Material and Methods

Sampling

Samples were collected from a cattle farm located 15 km East of Madrid in an economically depressed area. The farm is located in the surrounding of a CWI, closed on 1995, and a newly constructed MSWI which started operating in 1995. In close proximity there is a busy high-way, and a secondary road driving to the CWI and the MSWI area with a heavy traffic of Diesel tracks. This farm is approximately at a distance of 2.3 km from the MSWI, 3.3 km from the CWI, and 5.5 km from the high way.

Milk samples were taken from 11 cows in different periods, 1995 and 1998, during the lactating period, when their milk production is the highest. Milk samples from each sampling period were pooled . Six out of the eleven milk samples collected in 1998 were from the same cows than it was taken on 1995.

In spring and summer, the cattle mainly graze freely in pastures very closed to both incineration plants, while the rest of the year their main food is fodder.

Extraction and cleanup

Amounts of 200 ml of homogenated milk were layered-frozen at –78ºC for a better removal of water during the liofilization process. Approximately 20 g of powder milk were manually ground and mixed with 5 g of silica gel, and aprox 20 g of anhydrous sodium sulphate. This mixture was extracted with 300 ml of Acetone/Hexane (1:1 v/v).

The cleanup process consisted of a series of chromatographic columns. The first column was consisted of three layers in the following sequence from bottom to the top : silica, 44% H_2SO_4 on silica, and anhydrous sodium sulphate. The hexane eluent from this column was concentrated and submitted to a second column consisting of Florisil ® which was eluted with 150 ml of hexane (fraction a) and 250 ml of dichloromethane (fraction b). The PCDD and PCDF congeners were collected on fraction b.

Quantification

Resolution and quantification of PCDDs and PCDFs were performed by HRGC-HRMS using an AutoSpec Ultima (VG Analytical, Manchester, UK) coupled to a Fisons Series 8000 (8060) gas chromatograph. A fused silica capillary DB-5 column (60m, 0,25 mm i.d., 0,25 μm film thickness, J & W Scientific, USA) was used. Helium at a column head pressure of 175 KPa was used as the carrier gas. A minimum resolution of 10,000 was used when operating with the HRMS instrument.

Results and discussion

Table 1 presents average levels for all 17 2,3,7,8-substituted PCDDs and PCDFs in milk samples collected in 1995 and 1998. Total values were calculated assuming that "not detected" is equal to half the limit of detection. Almost all the seventeen congeners were found in both pools studied, except in the case of 1,2,3,4,7,8,9-HpCDF which was never detected. There is a noticeable difference between the two years studied. Total PCDD/F levels in milk samples collected in 1995 were found to be 45.84 ppt. This total value was found to be 10.42 ppt in 1998, approximately 4 times lower, indicating a clear decrease in exposure sources in the cows studied.

Table 1. PCDD and PCDF mean levels (pg/g on a fat weight basis) found in cow's milk during the two years studied.

	1995	1998
Total PCDFs	22.860	5.389
Total PCDDs	22.976	5.027
TOTAL PCDD/Fs	45.836	10.416
I-TEQ PCDFs	3.536	0.666
I-TEQ PCDDs	1.511	0.337
I-TEQ PCDD/Fs	5.047	1.003

Regarding total PCDDs and total PCDFs separately it can be seen that almost both groups contributed the half to the total PCDD/F levels, and this tendency can be observed in the two periods studied.

Figure 1 represents normalised concentrations for the 17 toxic congeners in milks from both periods studied. It can be seen that the congener pattern is similar in both periods studied, being the congeners with the highest contributions 1,2,3,4,6,7,8-HpCDD, OCDD, and 2,3,4,7,8-PeCDF. It should be pointed that there is a slight difference regarding OCDF which rise its levels in 1998 with respect to 1995.

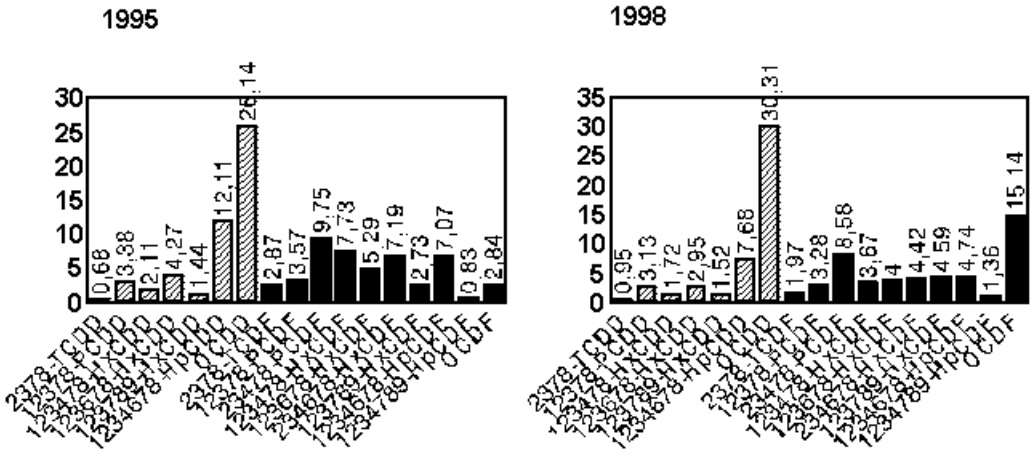

Fig.1 Normalised concentrations

Concerning I-TEQ levels, the total value found in 1995 was of 5.05 ppt, while levels found in 1998 were 1.01 ppt, 5 times lower.

Results seem to indicate that efforts to reduce PCDD/F emissions, such as optimisation of waste incineration technology, ban of production and use of pentachlorophenol in several countries, phasing out of leaded gasoline containing scavengers and substitution of chlorine in paper pulp bleaching with other reagents, are already beginning to have positive effects to a certain extent. This reduction seems to be mandatory in order to reduce PCDD/F levels in the environment as a prerequisite to diminish the body burden of humans (2).

Although in other works (3,4) it was observed that 2,3,7,8-TCDF and 1,2,3,7,8-PeCDF were found in very low levels in milk, in our study we have found relative high leveles of these congeners.

Figure 2 represents the normalised I-TEQ for the 17 toxic congeners in milks from both periods studied. It can be seen that although I-TEQ levels in 1998 are 5 times lower than in 1995, the contribution of each congener to the total I-TEQ is almost the same in each period. It is 2,3,4,7,8-PeCDF the congener with the highest contribution to the total I-TEQ levels with a percentage contribution of 45%.

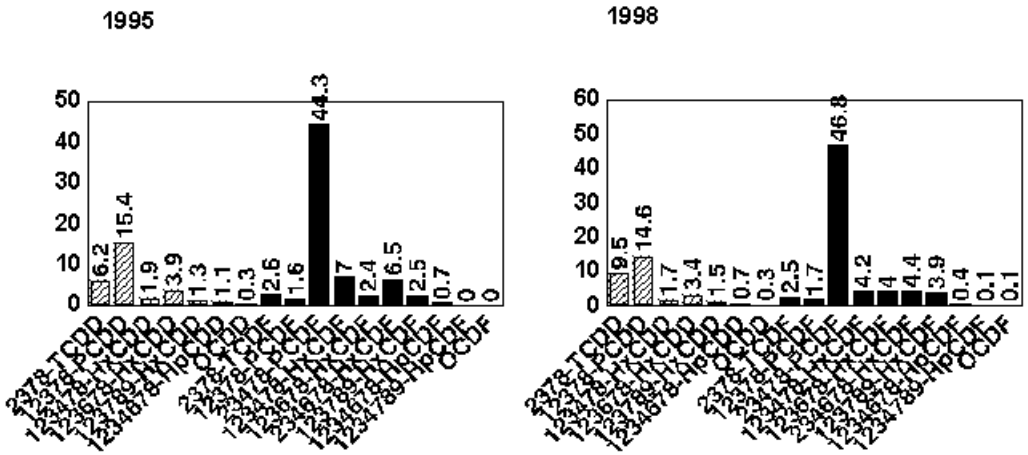

Fig.2 Normalised i-TEQs

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