LEVELS OF PCDDs AND PCDFs IN FARM COW'S MILK LOCATED NEAR POTENTIAL CONTAMINANT SOURCES IN ASTURIAS (SPAIN). COMPARISON WITH LEVELS FOUND IN CONTROL POINTS AND COMMERCIAL PASTEURIZED COW'S MILKS.

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1. Introduction

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are a highly lipophilic group of global pollutants. Of the 75 possible PCDDs and 135 possible PCDFs, scientific interest has been centred on those with four or more chlorine atoms and among them, specially on congeners with chlorines in the 2,3,7,8-positions due to their higher toxicity[1)].
The sources of PCDD/Fs are predominantly anthropogenic, in particular resulting from the use of organochlorine chemicals and combustion processes. Thereby, effluents from the production of organochlorine chemicals and waste incineration have been considered as the main sources of these compounds. Nevertheless, new sources begin to be taken under consideration such as those connected to the paper manufacture[2,3)]. Nowadays, the identification of unknown PCDD/Fs sources and the evaluation of the emissions from those that are know but as yet are not fully characterised is one of the more interesting areas of research.
The PCDD/Fs recalcitrance made that once emitted these pollutants will circulate through the environment for some time. Their lipophility makes them to be strongly bioaccumulative in species at the top of the food chains, specially in humans. It is considered that around 90-95% of the intake of PCDD/Fs in humans is via the consumption of food, with air inhalation, soil intake and skin uptake constituting the balance[4)]. As a result, the evaluation of the PCDD/Fs levels and the characterisation of their patterns in milk from dairy cows grazing near potential sources of these pollutants, and their comparison with those found in similar control samples and commercial samples is an interesting concern in order to determine the potential health damage to humans of this indirect via of exposure.
The aim of this study was to investigate the possible variations of the PCDD/F levels or patterns in cow's milk from farms in the vicinity of potential emission PCDD/Fs sources. Potential point sources are: a waste incinerator (WI), a chemical manufacture (Ch.M), three paper manufactures (P.M.), and a metallurgical plant (Mt.P.). The comparison of the levels found in these samples with those corresponding to the respective control points allowed to check the impact on the environment of the studied sources. Finally, the results were compared with those found in 15 samples of Spanish commercial pasteurised cow's milk from different brands, and with levels published for similar samples in other countries.

2. Materials and methods

Sampling

Different cow's milk samples were collected between February-April of 1995 in dairies near

Table 1. Pollution sources and distances to the farm investigated.

SYMBOL	POLLUTION SOURCE	DISTANCE TO THE FARM (m)
W.I.	Waste incinerator	500
P.M.1	Paper manufacture	600
P.M.2	Paper manufacture	650
P.M.3	Paper manufacture	550
Mt.P.	Metallurgical plant	700
Ch.M.	Chemical manufacture	800

possible emission sources of PCDD/Fs. Table 1 shows the different pollution sources located in the vicinity of the farms where the cow's milk were collected and the distances to the pollution sources. One cow's milk control sample was collected for each studied source near the corresponding dairy but far away the influence area of the source under consideration.
In addition, 15 commercial pasteurised cow's milks, from different brands, usually taken by the Spanish population were purchased from a supermarket.
<u>Analysis</u>
A 20 g freeze dried cow's milk was mixed with 42 g of 1:1 (w:w) silica gel:anhydrous sodium sulphate powder. The mixture was ground to become a fine powder, loaded into a column and spiked with a mixture containing 15 $^{13}C_{12}$ labelled 2,3,7,8-substituted PCDDs and PCDFs. Extraction was carried out with 300 ml of 1:1 (v:v) acetone:hexane mixture.
Fat was determinated gravimetrically and then dissolved in hexane and removed by elution of the extract through a glass column containing acidic silica with 44% concentrated sulfuric acid. The eluate was concentrated and transferred to an activated Florisil column (4501C, 24h) for final purification and separation of the PCDD/Fs from the PCBs.
One method blank was included for each five samples. Blank levels were negligible.
Sample extracts were analysed by HRGC/HRMS at 10,000 mass resolution on a VG AutoSpec Ultima (VG Analytical, Manchester, UK) equipped with an Electron Impact only source coupled to a FISONS series 8000 GC system. Acceleration voltage was 30 eV. Chromatography was run on a DB5, 60 m long, 0.25 mm i.d., 0.25 :m film thickness column. Helium was used as carrier gas. A 2 :l sample was injected in the splitless mode. The two major ions of the molecular ion cluster were monitored for each compound.

3. Results and discussion

Results summarised in Table 1 show that in general in all samples PCDD levels increased from T_4CDD to OCDD with the exception of the 1,2,3,7,8-P_5CDD. However, in the case of the PCDFs any general trend was observed.
In all cases the levels of 2,3,7,8-T_4CDD was lower than that of 2,3,7,8-T_4CDF, whereas the 1,2,3,7,8-P_5CDD level was between those of 1,2,3,7,8-P_5CDF and 2,3,4,7,8-P_5CDF. Except in commercial pasteurised cow's milk the levels of H_6CDDs and H_7CDDs were lower than those of H_6CDFs and H_7CDFs, whereas the levels of OCDD was clearly higher than that of OCDF (between 2.1 and 15.9 times higher).
Of the different studied sources only the WI seemed to have an influence over the PCDD/F levels found in cow's milk. The levels found in the WI sample were higher than those in its corresponding control point from P_5CDD/Fs to OCDD/F. The T_4CDD/F levels were very similar in both cases.

Table 2. Levels of PCDD/Fs in the different cow's milk samples analyzed (pg/g fat weight) and pg I-TEQs/g fat (. Results for commercial pasteurized cow's milks (COMM. MILK) is given as a mean (X) of the 15 individual samples and their.corresponding standard deviation (SD)

SAMPLE	WI	CONTR WI	PM 1	PM 2	PM 3	CONTR. PM	Mt.P	CONTR Mt.P.	Ch.M	CONTR Ch.M.	COMM. MILK	
											X	SD
2378-T_4CDF	1.28	1.15	1.13	1.07	1.02	1.28	1.39	1.20	1.78	1.58	0.34	0.67
2378-T_4CDD	0.36	0.32	0.09	0.17	0.15	0.18	0.25	0.14	0.47	0.14	ND	-
12378-P_5CDF	0.42	0.21	0.19	0.12	0.21	0.23	0.26	0.34	0.26	0.26	0.18	0.43
23478-P_5CDF	3.03	1.78	0.77	0.76	1.01	NQ	2.32	2.10	3.42	1.73	0.97	1.15
12378-P_5CDD	1.28	0.63	0.37	0.38	0.61	NQ	0.60	0.43	1.07	0.59	0.36	1.25
123478-H_6CDF	1.22	0.70	0.58	0.47	0.47	0.91	1.12	0.80	1.28	0.79	2.04	2.43
123678-H_6CDF	1.14	0.79	0.42	0.39	0.47	0.44	0.73	0.70	1.23	0.69	1.16	1.33
123789-H_6CDF	0.60	0.30	0.33	0.25	0.53	0.28	0.27	0.28	0.25	0.26	NQ	-
234678-H_6CDF	1.11	0.69	0.38	0.30	0.50	0.52	0.72	0.60	1.16	0.69	1.21	1.80
123478-H_6CDD	0.55	0.30	0.23	0.22	0.41	0.29	0.26	0.17	0.43	0.31	0.24	0.60
123678-H_6CDD	0.88	0.56	0.43	0.38	0.60	0.58	0.53	0.38	0.92	1.32	8.93	27.85
123789-H_6CDD	0.73	0.35	0.24	0.18	0.56	0.32	0.25	0.25	0.38	0.42	15.8	50.15
1234678-H_7CDF	0.80	0.43	0.51	0.32	0.43	0.43	0.57	0.54	0.64	0.62	7.21	6.58
1234789-H_7CDF	0.51	ND	NQ	ND	0.28	ND	ND	ND	ND	ND	0.23	0.79
1234678-H_7CDD	1.53	1.44	1.16	1.05	1.14	1.11	1.22	1.42	1.61	2.92	5.93	7.41
OCDF	2.66	0.62	1.91	0.45	0.89	0.51	0.57	0.58	0.56	0.80	8.55	15.3
OCDD	5.59	7.80	5.73	5.32	4.86	5.23	6.68	7.62	7.18	10.67	135.9	188.0
I-TEQ	3.32	2.04	1.06	1.09	1.45	0.67	2.27	1.88	3.50	1.90	3.80	

ND: No detected
NQ: No quantified (< 3 Detection Limit)

Some influence over the levels of certain congeners of P_5CDD/Fs and H_6CDD/Fs and specially for 2,3,7,8-T_4CDD level was found in the case of the Ch.M. The levels of these congeners were higher in the sample near the Ch.M. than in its corresponding control. Nevertheless, the levels of the rest of the congeners were very similar in both samples.

No significant differences were found between the PCDD/F levels in P.M. and Mt.P. samples and their corresponding controls.

Some important differences among the patterns of these samples and that found for the commercial pasteurised cow's milks was observed. Instead T_4CDD/F and P_5CDD/F levels were higher in samples from dairies than in commercial milks, the contrary was observed for the rest of the congeners.

Data obtained from the analysis of the commercial pasteurised cow's milks reveal H_6CDD, H_7CDD and OCDD as the more abundant congeners. In general these results agree with those found in the literature for similar kind of samples[5-7]. A wide variety was found for the PCDFs. In this case, OCDF and 1,2,3,4,6,7,8-H_7CDF were clearly predominant in the Spanish commercial pasteurised cow's milks while P_5CDFs and H_6CDFs seemed to be the more abundant congeners in the samples from Sweden[6] or Switzerland[7].

The results expressed in pg I-TEQ/g fat (I-TEF system) shows that milk samples obtained from the 10 farms studied (those near possible pollution sources and their corresponding controls) and the 15 commercial pasteurised milks (Table 2), contained concentrations of PCDD/Fs in the milk broadly within the range of 0.67 to 3.80 pg TEQ/g fat. Thus all of them are below the 6 pg TEQ/g fat which are the limit value for human consumption in the legislation of some European countries such as German, Holland and Austria. The I-TEQ of cow's milk from farms near possible pollution sources were always slighter higher than its corresponding control farm. The values of I-TEQ found in commercial milk (3.80 pg I-TEQ/g fat) was higher than those found in any cow's milk.

4. References

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