

Study of PCDD/Fs, dioxin-like and markers PCBs levels in cow's milks collected in farms in the neighbourhood of municipal solid waste incinerators.

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Introduction

At the end of 2004, new maximum tolerable levels for dioxins in food and milk will be proposed within the European Union (EU). They will include the dioxin-like PCBs. Until now, the dioxin maximum level in milk was 3 pg WHO-TEQ/g of fat. Two proposals are made for this new maximum level including the dioxin-like PCBs, either 5 or 7.5 pg WHO-TEQ/g fat. This paper presents the results of a surveillance programme on PCDD/Fs, dioxin-like PCBs and markers PCBs (# 28, 52, 101, 138, 153, 180) concentrations found in cow's milks collected in France either in Brittany or Pays de la Loire in the neighbourhood of MSWIs. These two regions are the most important producing ones for bovine milk. The raw milk samples were collected over 10 months in 10 farms. 129 milk samples were analysed for this study. Several criteria were selected to choose the farms: the vicinity of a waste incinerator, the predominant winds and the population density. Four areas in the neighbourhood of municipal solid waste incinerators (MSWIs) were monitored for this study; two were located in Brittany and two in the Pays de la Loire region. The general purpose of the study is to evaluate new semi-continuous monitoring systems for MSWIs and to assess their impact on environment all along the year. Ultimately, it is intended to provide tools to manage potential dioxin sources in an appropriate way, in order to prevent any sanitary impact. A secondary purpose is to evaluate the safety of milk produced in a specific environment, with respect to their content in PCDD/Fs and dioxin-like PCBs and show it complies with the future EC regulation. Those results are reported here.

Materials and Methods

Samples

MSWIs: four incinerators were selected for this study. The two largest (incinerators A and B) are located in urban areas. They could respectively burn 2×9.5 and 2×9 tons of shredded waste per hour. The two smallest MSWIs (incinerators C and D) are in rural areas and had a capacity of 3

tons/hour and 2×4 tons/hour. They are all equipped with flue gas treatment and air pollution control.

Samples: the milk samples were collected in tanks twice a month in eight farms: farms A1 and A2 were located respectively at 10 km and 8 km of the incinerator A; farms B1 and B2 were 5 km and 7 km from incinerator B; C2 and C3 were positioned at 3 and 5 km from incinerator C and finally, farms D2 and D3 were both located 4 km from incinerator D. The study was held from February to November 2003. Two other farms were added in June 2003: farms C1 and D1 at respectively located at 2 km of MSWI C and D. The remote farms (A and B) were in urban areas and under the predominant winds (figure 1). All samples were refrigerated at 4°C for transportation and immediately analysed.

Extraction and clean-up

The extraction and clean-up methodology has been already described¹. In a few words, a mixture of 35 ¹³C-labelled internal standards (mimetic of the 17 PCDD/Fs, the 12 dioxin-like PCBs and the 7 marker PCBs) was added to a 100 mL milk sample. A mixture of saturated sodium oxalate was added to precipitate the proteins; then ethanol was included and the fat was extracted twice with pentane. The lipid fraction was determined gravimetrically. Clean up and separation processes were carried out using the classic liquid-solid adsorption chromatography with silica, Florisil and Carbo-pack/Celite. The solvents used for the elution were hexane and toluene.

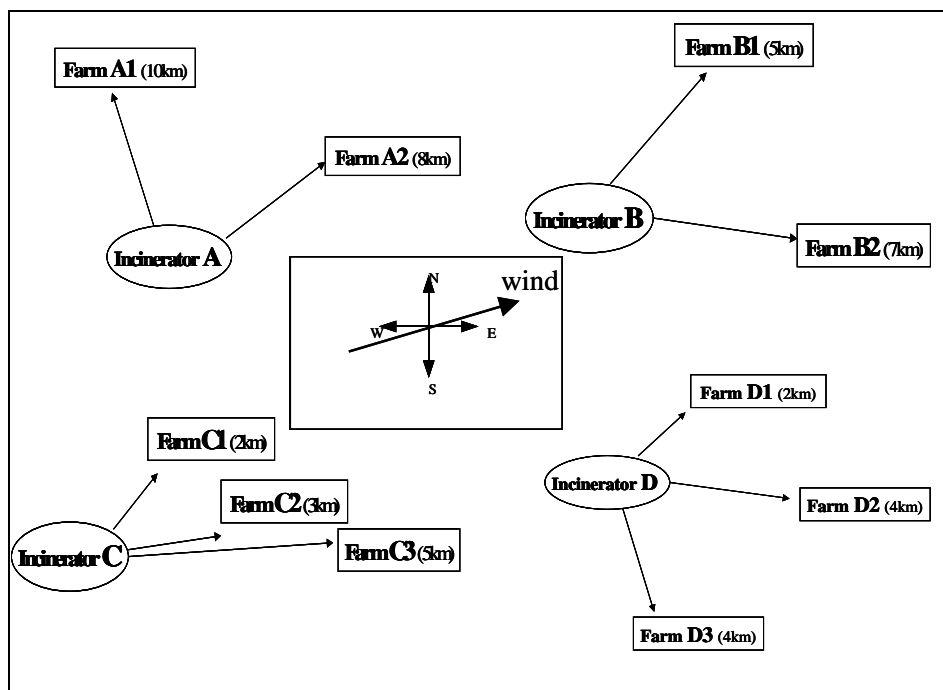


Figure 1. Farms localisations and predominant wind direction

GC/HRMS analysis

GC/HRMS analysis on the 17 dioxins, 12 dioxin-like and 7 marker PCBs was performed as previously described by Fürst¹. The congeners were separated by gas chromatography (GC) on a DB-5 MS capillary column (30 m×0.25 mm, 0.25 µm) and determined by high-resolution mass spectrometry (HRMS) on a JMS 700D (Jeol), at a resolution of 10000 in the selected ion-monitoring (SIM) mode using Electronic Impact as ionisation technique. TEQ values were calculated using WHO-TEFs.

Results and Discussion

Dioxin and Dioxin-like results

For each farm, 17 milks have been analyzed, except for the two latest farms (C1 and D1) including further in the protocol. The mean, maximum and minimum values are presented in Table 1.

Table 1: range of concentrations for dioxins, dioxin-like PCBs and their sum in the milk samples analysed (n=129).

	Km from MSWI	Farms	dioxins pg/g fat			dioxin-like PCBs pg/g fat			(dioxins+dioxin-like PCBs) pg/g fat		
			Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
City	10	A1 (n=17)	0.27	0.97	0.57	0.47	1.69	0.98	0.91	2.66	1.55
	8	A2 (n=15)	0.34	0.86	0.63	0.62	1.18	0.92	0.95	2.04	1.55
	5	B1 (n=15)	0.36	0.61	0.47	0.43	0.79	0.60	0.78	1.30	1.07
	7	B2 (n=15)	0.43	0.75	0.61	0.64	1.06	0.84	1.24	1.69	1.45
Countryside	2	C1 (n=8)	0.41	0.97	0.60	0.96	1.57	1.11	1.45	2.54	1.70
	3	C2 (n=16)	0.39	0.66	0.49	0.55	1.15	0.85	0.89	1.74	1.34
	5	C3 (n=16)	0.23	0.79	0.48	0.46	0.93	0.66	0.71	1.72	1.14
	2	D1 (n=6)	0.32	0.46	0.37	0.55	1.00	0.69	0.90	1.32	1.06
	4	D2 (n=15)	0.31	0.57	0.43	0.61	0.97	0.79	0.57	1.53	1.15
	4	D3 (n=15)	0.24	0.44	0.34	0.35	0.80	0.56	0.65	1.07	0.90

Two groups of farms come out: the first includes farms A and B and the second group includes all the others. Three of the four greatest concentrations in dioxins and dioxin-like PCBs correspond to the first group. The former group corresponds to the large population areas and the biggest incinerators. The results certainly illustrate more the urban effect than the incinerator effect. The latter group (farms C and D) corresponds to the smallest MSWIs and the countryside areas. For the farms in the neighbourhood of the waste incinerator C, the influence of the distance between the MSWI and the farm is sensitive: larger the distance is, higher the concentrations. The values obtained for the farms very close to the incinerator D don't support that remark: no distance effect is observed. The concentration depends on the predominant wind: farm D3 which is not under this flow showed lower concentrations than farms D1 and D2 which were more under the influence of the predominant winds.

This tends to demonstrate a city/countryside effect. For a distance higher than 5 km between a farm and a waste incinerator the contamination due to this MSWI can be considered insignificant. As a result, the values obtained for dioxins and dioxin-like PCBs for the farms around A and B do not represent the incinerator effect but the combustion emissions of the town. At the opposite, in the countryside, the results obtained for the samples collected in farms C and D demonstrate that the principal source of dioxin contamination was probably due to MSWIs.

The dioxin levels are contained in between 0.27 and 0.97 pg TEQ/g of fat. It is below the target value recommended by the European Union (1 pg WHO-TEQ/g l.w.) (Figure 2).

Figure 2 shows a variation of the dioxin concentration in the course of months: for all samples, we observe a decrease of the results till June or July 2003, then an increase until November 2003. This trend has already been observed². This points out that the monitoring of PCDD/Fs PCBs in milk should be carried out during autumn or wintertime to measure the apex of the maximum contamination in milk.

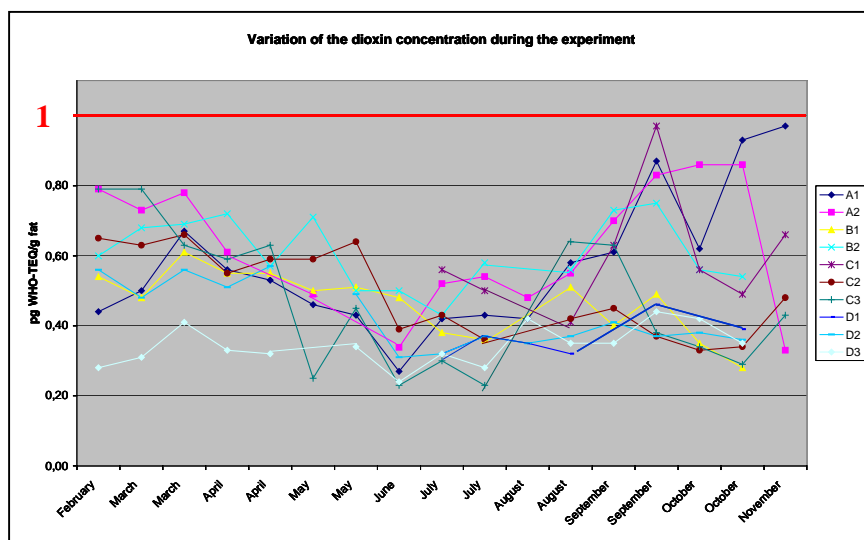


Figure 2 : variation of the dioxin concentration during the experiment (pg WHO-TEQ/g fat).

Since 2001, the EU maximum tolerance level for PCDD/Fs in dairy products is 3 pg WHO-TEQ/g fat. At the end of the year, a new limit will include the dioxin-like PCBs (5 or 7.5 pg WHO-TEQ/g fat). The sum of the dioxin and dioxin-like PCB concentrations calculated for all the samples analyzed in this study reached a maximum of 2.54 pg WHO-TEQ/g l.w which remained under the EU maximum tolerance level for dioxins alone (Figure 3). This demonstrates that the future limits proposed are realistic.

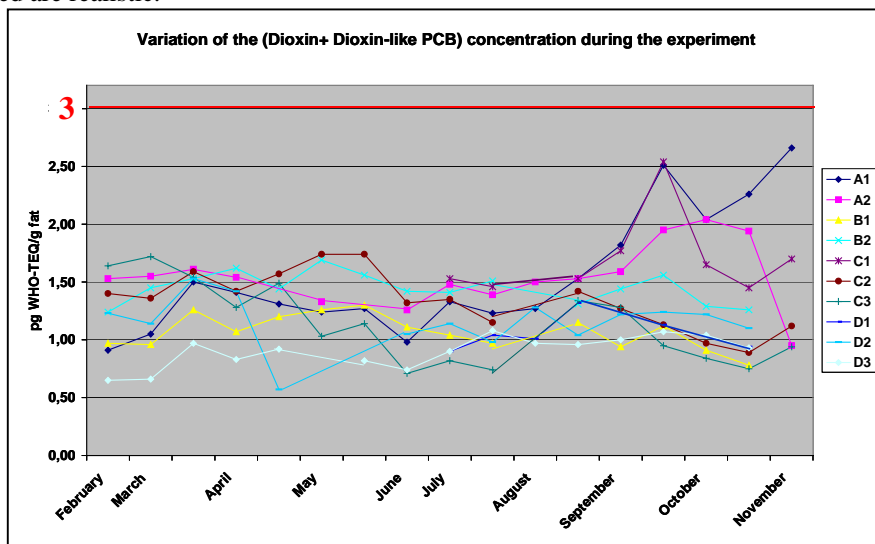


Figure 3 : variation of the (dioxin+dioxin-like PCB) concentration during the experiment (pg WHO-TEQ/g fat).

Statistical analysis

As an additional point, we studied a possible correlation in between dioxin and dioxin-like PCB concentrations. Figure 4 illustrates this parallel through the example of the farms close to the waste incinerator C. We notice a difference between the three farms: closer to the incinerator the farm was located, greater the ratio dioxin-like PCBs/dioxins was found. This has already been observed in this region³ and correlated to the location of the farms: not so far from one potential source of dioxins in a non-urban and non-industrial area.

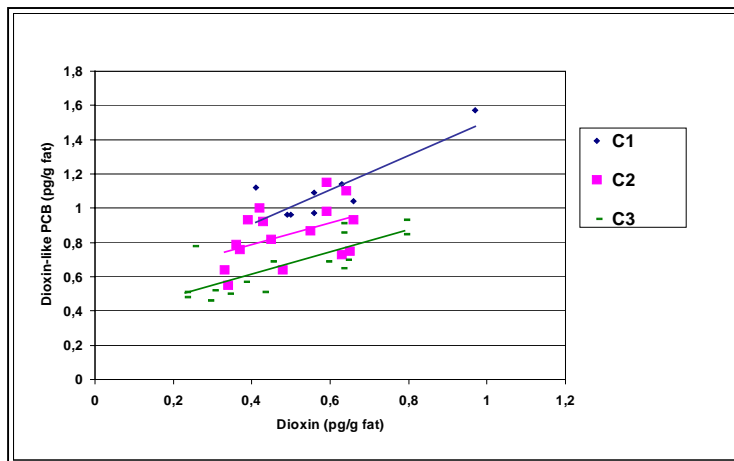


Figure 4: Correlation between dioxin and dioxin-like PCB results for farms C1, C2 and C3.

The second studied correlation was the relation between marker PCBs and dioxin-like PCBs. The concentrations obtained for the markers are gathered in the following table. The figure shows a good correlation between the variables ($R^2=0.746$).

Marker PCBs ng/g fat		
Farms	min	max
A1 (n=17)	2.14	6.41
A2 (n=15)	2.82	5.14
B1 (n=15)	2.08	4.17
B2 (n=15)	3.38	5.10
C1 (n=8)	4.00	6.98
C2 (n=16)	2.91	7.48
C3 (n=16)	2.23	3.93
D1 (n=6)	2.02	5.52
D2 (n=13)	3.01	5.19
D3 (n=15)	1.38	4.74

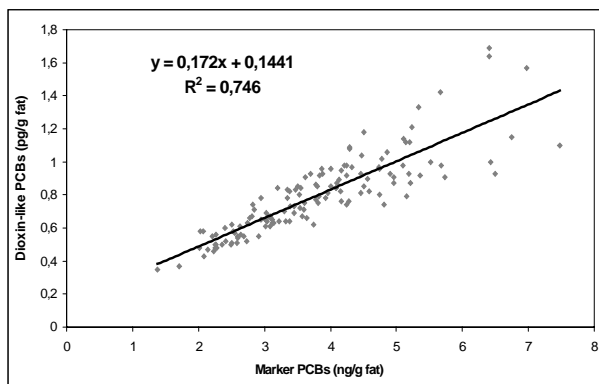


Table 2.: Marker PCB concentrations and **Figure 5.:** Correlation between dioxin-like and marker PCBs.

Conclusion

Whatever the considered farm (close to a city, in the countryside, at variable distance from an incinerator), all analysed milk samples collected in west of FRANCE showed concentrations below the target value of 1 pg WHO-TEQ/g l.w for dioxins; the sum dioxins plus dioxin-like PCBs, was found under the 3 pg WHO-TEQ/g fat level. The future maximum levels seem to be realistic according to this study. A seasonality of the concentrations has also been observed and

should be taken into account for the control programmes. Further analysis of other environmental data yielded in this study should provide tools for a more finely tuned monitoring system of environmental impact.

Considering waste incinerator C, the milk contamination was demonstrated to be dependant of the distance between the farm and the incinerator. The dioxin and PCB levels for the milks from farms A and B seem to be due to the industrial and urban activities.

A good correlation between the dioxin-like PCB and marker PCB concentrations for all the milk samples was observed and could lead to a new screening approach. These preliminary results recorded over a whole year period already show that correctly run MSWIs have little impact on food chain and are compatible with future EC dioxin regulation in food chain.

Acknowledgment

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