GC-MS Isomer-Specific Determination of PCBs and Some Chlorinated Pesticides in Milk and Cheese Samples.

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1. Introduction

Polychlorobiphenyls (PCBs) are ubiquitous pollutants with strong environmental persistency and tendency to biaccumulate.
It has been estimated [1] that some 1,200,000 tons of PCBs have been produced worldwide before they were banned from production. Their synthesis was based on batch chlorination of biphenyl, which yielded complex mixtures. The congeners with medium-high chlorine content (P_5CB, H_6CB, H_7CB), are prevalent in the animals at the top of the food web as a consequence of biomagnification.
Concern is increasing about food contamination by PCB congeners. The PCB congeners which can reach a planar conformation, show dioxin-like toxicity: for them Toxicity Equivalency Factors (TEFs) based on dioxin toxicity have been proposed[2,3,4]. Altough PCBs have TEFs from one to five orders of magnitude lower than that of 2,3,7,8-T_4CDD, their concentration in some matrices may be correspondingly higher, to balance the lower toxic potency [5,6]. Moreover other PCB congeners show other kinds of toxic effects, as immunotoxicity or neurotoxicity[1,3]; reproductive failure of seals living in polluted seas is suspected to be related to the high levels of PCBs[7].
It is then advisable to determine the PCBs as individual congeners, although they are always present in the environment as complex mixtures, whose composition patterns vary as a function of the analyzed matrix[8].
Milk and dairy products are one of the main contributors to the human intake of organochlorine compounds, and it is of interest to study both the their contamination level and the route of dairy cattle exposure to such products.

2. Materials and methods

The analytical procedures for the milk and cheese samples were briefly described in a previous paper[8]. They are based on the use of CG-MS with isotope dilution. The following fully ^{13}C labelled spikes were used: 2,4,4'-T_3CB (28); 3,3',4,4'-T_4CB(77); 2,2',4,5,5'-P_5CB (101); 3,3',4,4',5-P_5CB (126); 2,2',4,4',5,5'-H_6CB (153); 3,3',4,4',5,5'-H_7CB (169); 2,2',3,3',5,5',6 -H_7CB (178); HCB; DDT; DDE.
In order to assess the method precision and accuracy, the whole analytical procedure was applied 9 times to a single milk sample[9]. The relative standard deviations for 14 PCB congeners and the three pesticides vary almost regularly from 5% at a level of 180 pg/g to about 20% around 5-10 pg/g. With the only exception of HCB, the labelled spike recovery yields are higher than 75%.

Fifteen cheese samples, together with the milk used to produce them, were obtained from family size cheese producing farms in Valsassina, northern Italy. The farms owned between 11 and 25 cows each. The presence of industrial activities in the area surrounding each farm was checked and recorded. Four sample collections were performed: the first two during summer and the second two during winter. In the summer, the cattle was brought up in the mountains, freely grazing in the meadows, whilst in the wintertime it was fed with variuos types of fooder. These samples were collected within a National research project on the quality of dairy products; the study of trace elements on the same samples is in press[10]; in the same study the process of cheese making used is described in detail. Four milk samples were obtained from selected medium-to-large size dairy farms, suppliers of nationwide milk firms.

3. Results

The analytical method used allows the determination of 5 to 25 different PCB congeners, for concentrations of total PCB going from 4 to 100 ng/g fat; the non-ortho substituted congeners are not determinable, but mono-ortho congeners such as Nos. 105, 118, 156, which account for a significant share of equivalent toxicity, are.
The total PCB content is determined as sum of all determinable congeners; all major components are quantitated, and so the total PCB content is very slightly underestimated.
The PCB contamination levels (on fat basis) of the milk and cheese samples from Valsassina are constantly lower in the winter samples than in the summer, despite the fact that cattle, during the latter season, is grazing in presumably low contaminated sites. Moreover, summer milk has a higher fat content than the winter one.The winter milk samples show a mean PCB concentration of 43 ng/g (on fat basis), whilst the cheese samples have a mean PCB contamination of 38 ng/g fat ; the summer milk and cheese samples have a PCB mean concentration of, respectively, 68 and 71 ng/g fat. In Table1 only results on milk are listed.

4. Discussion

The contamination profiles of a single milk and of its corresponding cheese do not

FIGURE1: PCB congener profile of a cheese sample and of the milk used to produce it

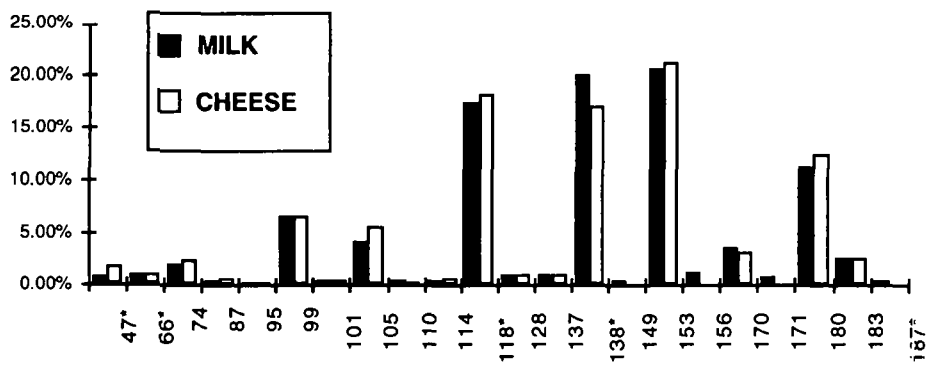

exhibit significant analytical differences (Figure 1); anyway, all milk and cheese samples analyzed in this study display a PCB contamination profile very similar to each other: the PCB contamination profile is not specific of a single milk or cheese sample.
Mean samples from different producers of the same area (Table1) show mesurable differences in contamination levels. Summer and winter samples from the same producer show even greater differences.
The excretion of PCBs via milk is the main elimination pathway of these compounds for cows. The excreted amount is proportional to the dose assumed[11] and reaches a maximum in a short time after ingestion: 1 day[12] or 1-3 days[13]. So, if the intake of PCB is not constant, also their excretion can vary sensibly even in a short time.
Generally, lower chlorinated congeners are more readily metabolized. Also the chlorine substitution pattern influences the rates of metabolism of PCB congeners: the presence of chlorine atoms in the 4 and 4' positions impairs the metabolic degradation of these compounds in cows[12] . This can be one of the reasons why the PCB contamination pattern of milk is rather different from environmental matrices[8], and can also partially explain why PCB contamination patterns of different milk samples are very similar.
In order to get some reference value of PCB contamination levels of the Italian milk, we have determined (Table1) PCBs in milk samples from four middle and large size milk farms from different regions of Italy (Lombardia, Toscana, Emilia, Veneto); it ranges from 5 to 15 ng/g fat; one previously analyzed commercial sampled had 23 ng/g fat[9];literature data are also generally lower than the Valsassina samples. The ratios of total PCB to DDE and HCB of the Valsassina milk samples are generally higher than other Italian samples . This may suggest that a specific pollution source of PCB exists for the Valsassina milk.
Further research is in progress to investigate on the origin of this source.

Table1. Concentration of some chlorinated compounds in milk samples from five small producers of Valsassina and from four medium-large size producers from different regions of Italy.

Milk	Prod.1	Prod.2	Prod.3	Prod.4	Prod.5	Lomb.	Tusc.	Emil.	Vene.
Samples*	3	3	3	3	3	1	1	1	1
DDE	8.4	7.8	8.8	16.3	9.9	7.9	0.6	8.1	21.7
HCB	5.7	5.9	8.3	6.3	5.5	2.2	0.4	3.6	2.4
PCB Tot	54	57	83	38	46	8.1	4.7	6.6	15

ng/g fat

*Each sample is a pool of the milk of all the cows in the farm.

5. References

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