Levels of Polychlorobiphenyl Congeners in Mean Diet Samples from Different Italian Areas

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Introduction

The composition of the diet in different areas of Italy may vary markedly; the same food may be cooked in different ways and with different ingredients. An example of a cooking practice that can significantly contribute to organohalogen compound intake is the use of animal fat instead of vegetable oil for frying. Culinary habits are reluctant to changes and resist to standardization.

Samples of regional reference diets prepared by the Istituto Nazionale per la Nutrizione (INN, National Nutrition Institute) for nutritional research purposes were analyzed in our laboratory in order to investigate whether the reference diet samples could be used to grossly assess the dietary intake of organic micropollutants.

Materials and Methods

Diet samples preparation: the samples were prepared by the INN according to the composition determined on a 10,000 household survey described in (1); shortly, 129 food items belonging to 11 main classes were used to represent the mean diets of four different Italian areas: North-western, North-eastern, Central, Southern. A National diet sample was also prepared. The various items were cooked according to the prevailing local habits. It is important to notice that industrial products of nationwide brands were the same for all the diets, whilst fresh products, such as fish, meat, bread, vegetables and fruits were bought locally, sometimes from a single shop. In this way some of the products included in the samples have a limited representativity for microcontaminant levels. A five-day sample (about 8.5 Kg) was prepared for each diet.

The North-western sample was prepared in 1992, the North-eastern and the Southern ones in 1993, whilst the Central and the National samples were prepared in 1995.

The samples were homogenized, and a one-day subsample (for a total amount varying from 1595 to 1773 g) was used for organic micropollutant determination; it was spiked with a solution containing a mixture of isotopically labeled internal standard. Eight deuterated polycyclic aromatic hydrocarbons (PAH) were used for all the samples, together with 8 fully ^{13}C labeled polychlorobiphenyl (PCB) congeners, four ^{13}C labeled chlorinated pesticides, 5 fully ^{13}C labeled polychlorodibenzodioxin (PCDD) congeners and 4 fully ^{13}C labeled polychlorodibenzofurans (PCDF) congeners. For the two samples prepared in 1995, 14 fully ^{13}C PCB and 5 fully ^{13}C labeled PCDF congeners were used.

The homogenized sample was immediately freeze-dried and stored until extraction. The extraction procedure was different for the three earlier samples: they were solvent-extracted with a multi-stage procedure using acetone and mixtures *n*-hexane/acetone 1:1 vol., followed by acetone evaporation, water washings in a separatory funnel and concentration to 500 ml; the two late samples were extracted by means of a Dionex ASE (Accelerated Solvent Extractor), 200 apparatus, using distilled *n*-hexane/acetone 1:1 vol. at 100 °C.

A portion of the final extract, in *n*-hexane solution, was then passed through concentrated sulfuric acid adsorbed onto an inert support column (Extrelut, MERCK), further purified on a multi-layer column, concentrated and analyzed by GC-MS.

The three earlier samples were analyzed together during 1995, whilst the two later samples were analyzed during 1998.

In this paper, only the results obtained on PCB and results on hexachlorobenzene (HCB) and on *p-p'*dichlorodiphenyldichloroethylene (DDE) will be reported, as results for PAH, for the first three diets, were already published (2) and analyses of PCDD and PCDF are still in progress.

In the GC-MS analysis 62 PCB congeners were searched, and about 45 were determined as previously described (3,4).

Each sample was analyzed in triplicate together with a procedural blank.

Results and Discussion

In Table 1 the results of the PCB analyses on the five diet samples are reported; data are expressed in ng/day for each homolog group and for total PCB. Also reported are the analytical mean coefficients of variation for triplicate analysis. The recovery yields for the isotopically labeled internal standard range from 66 to 84%.

Table 1. Intakes, ng/day, of total PCB, HCB and DDE; also reported are homolog group distribution of PCB.

	NAT.	C.	N.W.	N.E.	S.	ANALYTICAL C.V.
T_3CB, sum	175	194	208	285	235	10%
T_4CB, sum	498	428	595	663	752	7%
P_5CB, sum	540	500	1371	564	1131	5%
H_6CB, sum	621	682	1694	1814	2064	5%
H_7CB, sum	323	294	747	584	497	9%
O_8CB, sum	51	50	n.d.	n.d.	n.d.	6%
PCB, sum	2208	2147	4616	3910	4679	3%
HCB	318	275	210	208	173	10%
DDE	951	768	744	657	874	10%

n.d. = not determined

It is apparent that there are some striking differences which require some comments. In particular, the levels of hexachlorobiphenil, pentachlorobiphenyl and, partly, heptachlorobiphenyl congeners differ significantly in the various samples, and these differences account for most of the variation dispayed on total PCB.
This is probably due to the way samples were prepared: they were meant to be used for nutrition research purposes, and consequently priority was given to nutritional composition. Fresh food products were purchased in too little amount and too limited variety to wholly represent the variability of contamination of such food as meat, fish, milk or cheese. Meat and fish, for instance, were represented by 22 different items, each item in amount varying from 43,6 to 0.1 g per day. All the meat needed for one diet sample was often obtained from a single butcher shop, so representing the contamination of a single animal. On the other hand, it is known that PCB contamination differences of one order of magnitude are not rare among samples of the same foodstuff. It is then important to highlight that, from the micropollutant contamination standpoint, the representativity of the samples may be limited; on the other hand they are fully representative on the composition side. They can be considered as daily diet samples, having the mean local composition.
It is not surprising to notice that the Central and the National diets yield quite similar results: they were prepared together using the very same ingredients and their compositions are also alike. It is likewise worth noting that these two diets display the lower contamination from heavy congeners (5-, 6-, 7-Cl CB), suggesting that some important ingredient, such as cheese, butter or fish, with comparatively low contamination was used in their preparation. Animal fat is indeed rich on the heavy congeners. In Figure 1 the congener profile is shown for three of the samples displaying different homolog group distribution.
In our view in these samples the variability of contamination of the ingredients greatly prevails on compositional differences, and consequently the regional information is lost. Moreover the samples were prepared at considerably different times and there is in Europe a neat decreasing trend for PCB in Diets (5, 6). So, these data should not be used to compare regional Italian intakes.
However, they can be of use in order to grossly assess the range of PCB dietary intake in Italy: the two latest samples (National and Central, prepared in 1995) yield intake values comparable to those reported for 1994 Dutch diet (5).

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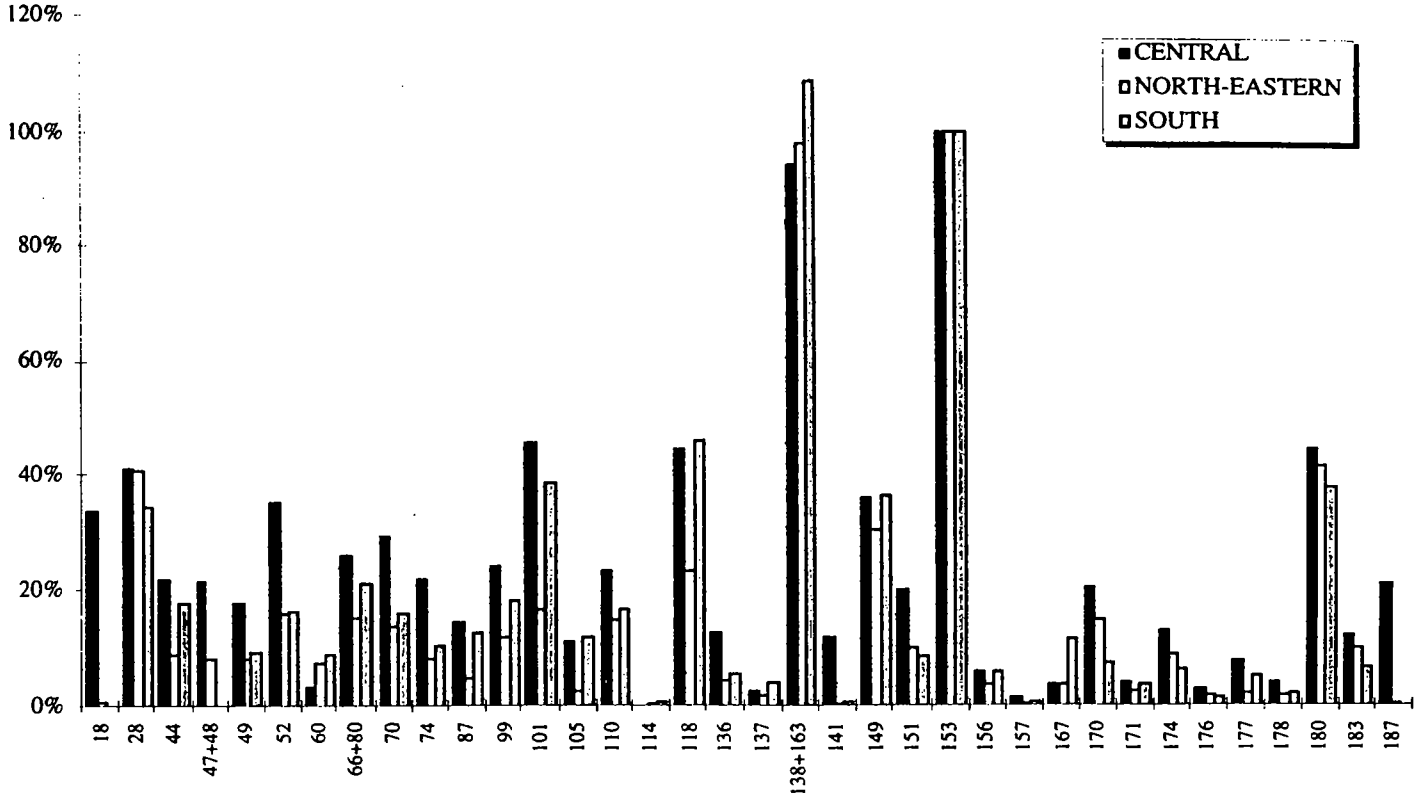

Figure 1. PCB congener profile of three samples showing significant differences in the homolog group distribution. H_6CB 153 = 100%.