# PCB congener profile and contamination levels of Italian National and regional diets.

## L. Turrio-Baldassarri, A. dl Domenico, N. Iacovella, C. La Rocca, M.G. Mediati, F. Rodriguez

Laboratory of Comparative Toxicology and Ecotoxicology, Istituto Superiore di Sanità, Viale Regina Elena 299, 00161 Rome, Italy

#### 1. Introduction

Culinary habits are among the components of national cultures which are most resistant to global standardization, and so national and regional diets may still vary consistently from nation to nation, and from region to region in the same country. In Italy many differences occur in the cooking habits of the various regions: a major example is the use of butter (north) or olive oil (south) as cooking oil.

Diet is the main route of human exposure to organochlorine compounds. Fatty foods with high content of animal fat, such as fish, meat, milk and dairy products are estimated to be the highest contributors of such compounds to human diet, whilst vegetable oils have a lesser importance in this respect. Polychlorobiphenyls (PCBs) are ubiquitous pollutants with strong environmental persistency and tendency to biaccumulate. The congeners with medium-high chlorine content ( $P_5CB$ ,  $H_6CB$ ,  $H_7CB$ ), are prevalent in the fatty tissues of animals at the top of the food web, as a consequence of biomagnification.

Concern is increasing about PCB food contamination, due to the different toxicities and potencies of the various 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<sup>(1,2,3,)</sup>. Altough PCBs have TEFs several orders of magnitude lower than that of 2,3,7,8-TCDD, their concentration in some matrices is often correspondingly higher, and so it balances the lower toxic potency<sup>(4,5)</sup>. Moreover other PCB congeners show other kinds of toxic effects, as immunotoxicity or neurotoxicity<sup>(2)</sup>. Reproductive failure of seals living in polluted seas is suspected to be related to the high levels of PCBs<sup>(6)</sup>.

In this paper results are presented on PCB determination in the Italian national diet; by the date of the symposium, data on three Italian regional diets will be also available.

#### 2. Materials and methods

<u>Mean Italian diet</u>: Food and beverages in proportion to their average daily consumption were purchased and prepared according to normal consumer conditions. The 1700 g daily diet sample had the following composition: cereals g 311; milk and dairy products g 250; vegetables g 285; fresh and dry legumes g 26; fresh fruits and nuts g 231; meat, fish and eggs g 205; beverages (including alcoholic ones) g 279; cakes g 50; fat and oil g 54; dressings g 8.

These components were finely and thoroughly homogenized and carefully freeze-dried. In these conditions the daily diet sample yielded 533 g of lyophilized sample. Its weight percent

composition was the following:  $H_2O$  5.84; proteins 18.82; lipids 16.48; soluble carbohydrates 15.4; starch 34.3; ashes 4.35; fibers 4.81.

Before the extraction the samples were spiked with a mixture of the following <sup>13</sup>C labeled standards: 2,4,4'-T<sub>3</sub>CB; 2,2',5,5'-T<sub>4</sub>CB; 3,3',4,4'-T<sub>4</sub>CB; 2,2',4,5,5'-P<sub>5</sub>CB; 3,3',4,4',5-P<sub>5</sub>CB; 2,2',4,4',5,5'-H<sub>6</sub>CB; 3,3',4,4',5,5'-H<sub>6</sub>CB; 2,2',3,3',5,5',6-H<sub>7</sub>CB. Isotopically labeled PCDDs, PCDFs and PAHs were also added.

On the dried sample the fat extraction was performed by overnight stirring with a 5:2 (v/v) acetone/*n*-hexane mixture. The extraction was repeated three times and the filtered extracts were pooled.Extractable fat turned out to be 15.25%.

A cleanup procedure originally set up for PAHs proved to be suitable also for the PCB determination. It involves, briefly, after partition with water to get rid of acetone and dehydratation with Na<sub>2</sub>SO<sub>4</sub>, partition between *n*-hexane and dimethylsulfoxide (DMSO) and back partition between acqueous DMSO and cyclohexane<sup>(7)</sup>.

	ng/g fat	ng/day		ng/g fat	ng/day
T3CB			H6CB	nd<0.45	nd<35
18	3	231	128	3	220
28*	11	850	129	nd	nd
T4CB	nd<0.35	nd<27	136	4	349
44	4	299	137	5	406
47*	2	123	138*	28	2214
49	2	155	141	4	305
52	8	586	149	15	1201
60*	3	251	151	4	323
66*	4	335	153	27	2094
70	6	478	156	3	264
77	nd	nd	157	nd	nd
P5CB	nd<0.4	nd<31	HŦĊB	nd<0.5	nd<40
87	5	376	170	7	509
95	10	752	171	1	108
99	3	266	174	4	323
101	11	851	176	nd	nd
105	4	310	177	1	41
110	14	1073	178	nd	nd
114	nd	nd	180	9	697
118*	10	741	183	3	243
122	nd	nd	187*	5	413
126	nd	nd	189	nd	nd
SumT3CB	14	1082	SumH6CB	95	7375
SumT4CB	29	2227	SumP5CB	56	4370
SumH7CB	30	2334	TotalPCB	223	17388

 Table 1.
 Levels of PCB congeners in the Italian mean diet.
 Results

 are listed both as fat based concentrations and individual daily intake
 Italian mean diet.
 Italian mean diet.

The asterisk labels the possible presence of coeluting isomers.

After treatment with  $Na_2SO_4$ , the concentrated residue was submitted to silica gel chromatography<sup>(8)</sup>. The eluate was subsequently made up to a 100-µl volume with an *iso*-octane solution of <sup>13</sup>C-labeled chlordane (injection standard). Individual PCBs were



Figure 1. PCB contamination profiles of Italian mean diet and Italian human milk.

HEX

ORGANOHALOGEN COMPOUNDS Vol.26 (1995)

123

quantitated by comparing their M<sup>+</sup> area with that of the relative labeled standard; correction for instrumental response was introduced through the pertinent RRF<sup>(9)</sup>. Quantitation was performed by HRGC-MS on a HP5989A instrument. The instrument was equipped with an on-column injector and an HP Ultra 2 capillary gas cromatographic column (50-m-long 0.32 mm-i.d.).Here only PCB results are reported.

#### 3. Results

In Table 1 the results of the determination of PCBs in the sample of the Italian mean daily diet are reported. Forty-one congeners are listed together with the total PCBs and the total for each isomer class. The results are expressed on both the fat based concentration and individual daily intake.

#### 4. Discussion

The congener contamination profile of the diet is made of a large number of relevant congeners. Some foods of animal origin show a simplified congener pattern, whilst environmental matrices feature high congener multiplicity<sup>(8)</sup>. This may imply that diet is largely contaminated by "first hand" pollution. The different congener multiplicity of the diet with respect to human milk, a high ranking food web item, is illustrated in Figure 1.

The PCB congener contamination profile of the Italian mean diet is compared to Italian pooled human milk: 41 congeners are represented in the bar graph, having from three to seven chlorine atoms. Each congener concentration is referred to the concentration of the most abundant, made equal to 1. The higher number of relevant congeners of the diet is clearly visible. Incidentally, the difference between the two profiles of Figure 1 may be attributed to the human metabolic activity.

### 5. References

- 1. Safe, S. (1990) Critical Rev. Toxicol.21, 51-88.
- 2. Ahlborg, U.G., Hanberg, A., Kenne, K. Risk assessment of polychlorinated biphenyls (PCBs). The Nordic Council, 1992, Report Nord. 1992:26.
- Ahlborg, UG. Becking, GC. Birnbaum, LS. Brouwer, A. Derks, HJGM. Feeley, M. Golor, G. Hanberg, A. Larsen, JC. Lirm, AKD. Safe, S. Schlatter, C. Waern, F. Younes, M. Yrjänheikki, E. (1994) Chemosphere, 28, 1049-1067.
- 4 Larsen, B.R., Nilsson, T., Facchetti, S., Turrio Baldassarri, L., Iacovella, N., di Domenico, A., M. Montagna (1994) Ecotox. Environ. Safety, 28, 1-13.
- 5. Noren, K; Lunden , A(1991). Chemosphere , 23, 1895-1901.
- 6. De Voogt,P; Weels, D.E; Reutergårdh, L; Brinkman, U.A.T.(1990).Intern. J. Environ. Anal. Chem., 40, 1-46.
- 7. Natusch, D.F.S., Tomkins, B.A. (1978). Anal. Chem. 50, 1429-1434.
- 8. Turrio Baldassarri, L; di Domenico, A; Fulgenzi, A; Iacovella, N; La Rocca, C.(1993) . Sci. Total. Environ. Supplement 1993, 1439-1451.
- Turrio-Baldassarri, L., di Domenico, A., Fulgenzi, A.R., La Rocca, C., Iacovella, N., Rodriguez, F., and Volpi F. (1995). Influence of relative response factor variability in the determination of organic microcontaminants with isotopically labeled standards. Mikrochimica Acta, submitted for publication.