

Polychlorodibenzodioxins, Polychlorodibenzofurans, and Non-Ortho Polychlorobiphenyls in Human Milk: Concentration Levels and Time Trends in Italy

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Introduction

The analytical determination of PCDD+PCDF and dioxin-like PCB levels in human milk has been widely recognized to provide a reliable estimate of maternal body burden. It is also currently used to characterize breast-fed children exposure to these substances and the associated potential health risks, with particular attention to very sensitive toxicological endpoints as developmental effects.

Human milk samples of primiparous women living in the areas of Rome and Venice were collected in the period 1998–2001 and analyzed in order to provide an update of PCDD+PCDF, and non-*ortho* PCB levels in mother milk in Italy with respect to a previous work carried out in 1987 in four Italian cities (Florence, Milan, Pavia, and Rome),¹ and to describe the pertinent temporal trends. For the group of mothers from the Venice area, the role of fish consumption in determining maternal body-burden was also investigated. For this purpose, milk donors from Venice and surrounding areas were grouped on the basis of their fish consumption, and milk samples accordingly pooled prior to analysis.

Materials and methods

Sampling. Milk samples were obtained from primiparous women living in Venice, Rome, and their surroundings. Questionnaires documented dietary habits. Samples from Venice were collected between 1998 and 2000 from 29 mothers, with the assistance of local sanitary authorities. Individual samples were mixed to obtain three pools according with mothers' fish consumption levels (pool ID, number of donors in the pool, mean age): low consumption (LC), 10 donors, 31 years; medium consumption (MC), 13 donors, 30 years; high consumption (HC), six donors, 27 years. Samples from Rome were collected in the hospitals "Umberto I" and "San Giovanni-Addolorata" from 10 mothers over the period 2000–2001. The 10 individual samples were pooled together (mean age of donors, 34 years).

Analysis. Equal amounts of milk from individual mothers were mixed to constitute the pooled samples. Before extraction, each pool was spiked with ¹³C-labelled internal standards and freeze-dried. Lyophilized samples were Soxhlet-extracted with *n*-hexane, each lipid fraction was gravimetrically determined, and clean-ups were carried out by a multi-step procedure as described by Malisch *et al.*, 2000.² High-resolution gas chromatography coupled with high-resolution mass spectrometry in the selected ion monitoring mode (HRGC-HRMS(SIM)) was utilized for quantification of PCDD+PCDF and non-*ortho* PCB congeners.

Results and discussion

Table 1 summarizes the congener and cumulative concentrations of PCDDs+PCDFs and non-*ortho* PCBs measured in the Venice and Rome mother milk pools analyzed. Cumulative concentrations appear to range from 9.4–15 pgWHO-TEQ g⁻¹ lipid base (*lb*) and from 4.2–8.8 pgWHO-TEQ g⁻¹ *lb*, respectively. The concentration of the most toxic congener 2,3,7,8-T₄CDD spans over a range of 1.1–1.8 pg g⁻¹ *lb*. In general, PCDD+PCDF levels and profiles in Italy are in a good agreement with those reported for other European countries;^{3–9,11–13} higher levels were

sometimes reported for specific PCDD+PCDF congeners, such as 1,2,3,4,6,7,8-H₇CDD, O₈CDD, 1,2,3,4,7,8,9-H₇CDF, and O₈CDF.^{3,5,7-9} The PCDD+PCDF levels detected in Venice mother milk do not appear to be positively correlated with increasing fish dietary intake, as they possibly exhibit a negative trend. This is inconsistent with a recent study:¹⁰ we have no sound explanation for the inconsistency, aside from saying that, in our case, fish consumption was apparently compensated with that of milk and dairy products.

Contaminant concentrations in mother milk collected in various Italian areas over time were re-evaluated to yield indicative quantities for time comparison (Table 2). On average, the PCDD+PCDF cumulative level of 1998–2001 (12 pgWHO-TE g⁻¹ lb) seems to be some 60 % lower than the indicative estimate of 1987 (29 pgWHO-TE g⁻¹ lb).¹ Single congeners exhibit an average 66 % decrease. The decline affects primarily (>75 %) 2,3,7,8-T₄CDD, 1,2,3,4,6,7,8-H₇CDD, and 1,2,3,4,6,7,8-H₇CDF, and to the least (<40 %) 2,3,4,7,8-P₅CDF. Over the same period, the indicative non-*ortho* PCB cumulative value shows a decrease in the order of 52 % (from 14 to 6.8 pgWHO-TE g⁻¹ lb). The individual concentrations of non-*ortho* PCBs appear to be lower in 1998–2001 from 26 % (H₆CB-169) to 53 % (P₅CB-126). The decrease of PCDD+PCDF and non-*ortho* PCB concentrations observed between the periods reported above is in general agreement with the results found in other European countries.^{3-9,11-12}

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Table 1. PCDD, PCDF, and non-*ortho* PCB concentrations (pg g⁻¹ lb) in human milk pools from the areas of Venice and Rome.^{a,b} Values rounded off to two figures.

| Analytes | Venice LC | Venice MC | Venice HC | Rome |
|--|-------------------|-----------|-----------|-------|
| 2,3,7,8-T ₄ CDD | 1.8 | 1.5 | 1.3 | 1.1 |
| 1,2,3,7,8-P ₅ CDD | 4.2 | 3.7 | 3.3 | 2.8 |
| 1,2,3,4,7,8-H ₆ CDD | 2.4 | 2.6 | 2.5 | 1.7 |
| 1,2,3,6,7,8-H ₆ CDD | 12 | 11 | 9.2 | 7.1 |
| 1,2,3,7,8,9-H ₆ CDD | 3.3 | 2.6 | 2.2 | 1.6 |
| 1,2,3,4,6,7,8-H ₇ CDD | 16 | 15 | 13 | 11 |
| O ₈ CDD | 68 | 65 | 57 | 52 |
| 2,3,7,8-T ₄ CDF | 0.62 | 0.76 | 0.67 | 0.47 |
| 1,2,3,7,8-P ₅ CDF | 0.48 | 0.45 | 0.39 | 0.22 |
| 2,3,4,7,8-P ₅ CDF | 12 | 11 | 9.4 | 7.8 |
| 1,2,3,4,7,8-H ₆ CDF | 3.3 | 3.4 | 2.7 | 2.2 |
| 1,2,3,6,7,8-H ₆ CDF | 2.9 | 3.0 | 2.4 | 1.8 |
| 1,2,3,7,8,9-H ₆ CDF | <0.1 ^c | <0.2 | <0.3 | <0.05 |
| 2,3,4,6,7,8-H ₆ CDF | 1.3 | 1.6 | 1.3 | 0.89 |
| 1,2,3,4,6,7,8-H ₇ CDF | 1.7 | 1.7 | 4.4 | 1.1 |
| 1,2,3,4,7,8,9-H ₇ CDF | 0.056 | 0.094 | 0.13 | 0.063 |
| O ₈ CDF | 0.19 | 1.0 | 5.2 | 0.56 |
| T ₄ CB-77 | 7.1 | 9.9 | 9.7 | 4.3 |
| P ₅ CB-126 | 78 | 83 | 61 | 39 |
| H ₆ CB-169 | 54 | 52 | 36 | 31 |
| Σ(PCDDs+PCDFs, WHO-TEQs) ^d | 15 | 14 | 12 | 9.4 |
| Σ(non-ortho PCBs, WHO-TEQs) ^d | 8.3 | 8.8 | 6.5 | 4.2 |

(a) For the area of Venice, LC, MC, and HC indicate low, medium, and high consumption of local fish and fishery products.

(b) Extracted lipids: LC, 2.6 %; MC, 3.1 %; HC, 2.7 %; Rome, 2.9 %.

Concentrations on the lipid base (lb).

(c) The sign < indicates limit of quantification (LOQ).

(d) Medium bound approach. Estimated analytical uncertainty (CV%), ≈ | ±1–2 % |.

Table 2. PCDD, PCDF, and non-ortho PCB concentrations (pg g⁻¹ lb) in human milk sampled in Italy in 1987 and 1998–2001. The original outcomes were clustered, frequency weighted, and averaged. Values rounded off to two figures.

| Analytes | 1987 ^a | 1998-2001 ^b | Δ (%) ^c |
|---|-------------------|------------------------|--------------------|
| 2,3,7,8-T ₄ CDD | 6.3 | 1.4 | 79 |
| 1,2,3,7,8-P ₅ CDD | 8.2 | 3.3 | 60 |
| 1,2,3,4,7,8-H ₆ CDD ^d | 36 | 12 | 70 |
| 1,2,3,6,7,8-H ₆ CDD ^d | — | — | — |
| 1,2,3,7,8,9-H ₆ CDD | 7.3 | 2.2 | 70 |
| 1,2,3,4,6,7,8-H ₇ CDD | 63 | 14 | 79 |
| O ₈ CDD | 150 | 60 | 60 |

EMV - Body Burden and Dietary Intake

| | | | |
|--|-------------------|-------|-----|
| 2,3,7,8-T ₄ CDF | 2.4 | 0.63 | 73 |
| 1,2,3,7,8-P ₅ CDF | 0.84 | 0.35 | 58 |
| 2,3,4,7,8-P ₅ CDF | 16 | 9.9 | 38 |
| 1,2,3,4,7,8-H ₆ CDF | 5.5 | 2.9 | 48 |
| 1,2,3,6,7,8-H ₆ CDF | 5.7 | 2.5 | 56 |
| 1,2,3,7,8,9-H ₆ CDF | <0.5 ^e | <0.1 | — |
| 2,3,4,6,7,8-H ₆ CDF | 4.0 | 1.3 | 67 |
| 1,2,3,4,6,7,8-H ₇ CDF | 8.6 | 1.4 | 83 |
| 1,2,3,4,7,8,9-H ₇ CDF | <0.5 | 0.080 | <84 |
| O ₈ CDF | <2 | 0.82 | <59 |
| T ₄ CB-77 | 14 | 7.5 | 45 |
| P ₅ CB-126 | 130 | 64 | 53 |
| H ₆ CB-169 | 58 | 43 | 26 |
| Σ(PCDDs+PCDFs, WHO-TEQs) ^f | 29 | 12 | 60 |
| Σ(non-ortho PCBs, WHO-TEQs) ^f | 14 | 6.8 | 52 |

(a) Four pools/outcomes, from the areas of Florence, Milan, Pavia, and Rome.¹

(b) Two pools/outcomes, from the areas of Venice (MC) and Rome.

(c) $\Delta = \{[1987] - [1998-2001]\} \times [1987]^{-1} \times 100$.

(d) 1987 results given for the sum of 1,2,3,4,7,8- and 1,2,3,6,7,8-H₆CDD.

1998–2001 individual weighted values: 12 and 9.4 pg g⁻¹ lb, respectively.

(e) The sign < indicates limit of quantification (LOQ).

(f) Medium bound approach. Estimated analytical uncertainty (CV%), <|±20 %| in 1987 and ≈|±1–2 %| in 1998–2001.

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