# SERUM LEVELS OF PCDDs, PCDFs AND DIOXIN-LIKE PCBs IN RELATION TO DIFFERENT EXPOSURES IN ITALIAN ADULT MEN

Raccanelli S[1], Frangipane G[2], Libralato S[3]

[1] Consorzio I.N.C.A., VEGA-Edificio Cygnus, Via delle Industrie 21/8, 30175 Marghera (VE), Italy; [2] Ca' Foscari University Environmental Science Department, 30123 Venice, Italy; [3] Borgo Grotta Gigante 42/c, 34010, Sgonico (TS), Italy

**Abstract**

In the present work, first data on serum concentration of dioxins referred to Italian men with different exposure histories are presented, analysed and compared. One dataset regards samples collected in 1998 from Venice resident volunteers with main differences referred to dietary exposures associated to high or low local fish and shellfish consumption. The other dataset regards samples collected in 2007 from a group of people subjected to different exposure scenarios including individuals that have been subjected to occupational exposure. Preliminary main evidences highlighted the positive relationship between age and total dioxins TEQ levels. Moreover, data evidenced the association between higher PCBs total TEQ values to high fish consumers and workers employed in chemical plants of the Venice Lagoon.

**Introduction**

Human exposure to PCDDs, PCDFs and dioxin-like PCBs (dioxins) is a matter of concern for the presence of numerous anthropogenic sources of POPs. This is true particularly in highly industrialized and urban areas such as the Venice Lagoon, which, since decades, has been receiving discharges of many classes of pollutants from its drainage basin, from urban and industrial areas laying on lagoon borders and from the city itself. In particular, from the beginning of the 20th century, the adjacent mainland territory has been hosting one of the largest industrial area of Europe, namely the Porto Marghera Industrial Zone. Here a very broad range of activities and processes like non ferrous metal production, chemical industry (including PVC), municipal and hospital waste incineration, hazardous waste incineration, have been important sources of dioxins and dioxin-like compounds as well as other classes of pollutants that were released into the environment[1,2]. Dioxins have therefore been accumulating in lagoon sediments becoming potentially bioavailable to benthic communities and, consequently, entering the trophic chain [3]. Main concerns arise from the coexistence of pollution, from all the known sources, documented by data on sediment and biotic levels of pollutants, and a higher average local fish consumption with respect to national averages[4,5,6]. Concerns are strengthened by a previous preliminary study on the fate of dioxins in the Venice Lagoon, including analysis of their concentration in Venetian human breast milk[7]. In the present work, first data on serum concentration of dioxins referred to Italian men with different exposure histories are presented, analysed and compared. One dataset, collected in 1998, is particularly focusing on dietary exposures: two groups of venetian population were considered with respect to consumption of locally harvested fish and shellfish. Another set of data collected in 2007 regards a group of people subjected to diverse exposure scenarios and includes individuals that have been subjected to occupational exposure.

**Materials and Methods**

The first dataset (A) regards serum samples collected in 1998 from Venice resident volunteers[8]. In order to understand potential exposition to dioxins, a questionnaire focussing on life-style, general environmental and eating-habits was specially prepared and submitted to participants. Among the 41 selected volunteers, two groups were identified on the basis of their diet: 22 consumers of large amounts of locally caught fish and shellfish (at least 3 times a week), and 19 people consuming very little fish of any kind (less than 2 times a week). A blood sample of about 10 mL was taken from each individual. The second dataset (B) regards samples collected in 2007 and refers to 16 Italian volunteers with diverse exposure histories: six individuals have been employed for several years in chemical plants of Porto Marghera Industrial Zone, whereas for the others ten no particular concerns regarding their exposure life histories are known. A blood sample of 50 ml was taken from each individual in order to have two 10 ml samples of serum. In order to obtain suitable serum samples from whole-blood ones for dioxin analysis purpose, a specific protocol for collection, treatment and conservation of blood samples was rigorously

applied for both datasets[9]. Serum samples regarding dataset A were maintained frozen at –20°C till shipment to the laboratories of US- National Center for Environmental Health (Center for Disease Control- Atlanta) where subsequent treatments and analysis were performed. Samples regarding dataset B were treated and analysed at the POP Laboratory, Consortium INCA, Marghera, Italy.
Three replicates were analysed for each serum sample and for each batch of samples a blank (distilled water) and a quality control serum (human control, i.e. the SRM 1589a by NIST) were considered. The analyses were performed on serum extracted by an isotope dilution method using relative response factors previously obtained from five standard solutions injections, as recommended by the US-EPA[10,11]. PCDDs (7 congeners), PCDFs (10 congeners) and dioxin-like PCBs (4 congeners) were analyzed in samples regarding dataset A, whereas the quantitative determination of PCDDs/PCDFs, PCBs (12 dioxin-like and 17 other PCB) and HCB was performed for dataset B. Lipidic content of serum was analytically determined for normalization of dioxins levels to serum fat content.
For this work, the two data sets are compared taking into account only common measured congeners, i.e. only data regarding PCDD/Fs, PCB 77, PCB81, PCB126 and PCB169 are used. For analytical results below of the detection limits, a value equal to 0.5 of the detection limit referred to lipidic fraction was considered. Toxicity Equivalent (TEQ) levels were calculated using recent reassessment of WHO-Toxicity Equivalent Factors (WHO-TEFs) values[12]. These data are also compared with analogous serum measurements concerning the employees of an incinerator plant in the Northern Italy (Bolzano). These data were recently collected (2006) and regard concentrations of PCDD/Fs only (W. Tirler, Eco-Research, Bolzano, Italy; Communication at 6°CIND in Venice, Italy).

**Results and Discussion**
Data collected in the two datasets show a clear positive relationship between age of individuals and total TEQ values in serum. This is exemplified by Fig. 1, which presents the results for the total TEQ (PCDD/Fs+PCBs) and the fitting with the exponential function, y=A·exp(k·age). Contribution of PCBs and PCDD/Fs to total TEQ are reported in Table 1, which presents also the estimation of the doubling time (years needed for the total TEQ level to increase by a factor of 2). Results highlight a steeper increase of total TEQ values with age for PCBs than for PCDD/Fs, with doubling time of approximately 19 and 26 years, respectively. Although the increase of total TEQ levels with age is in full agreement with previous studies conducted in other countries, the wide heterogeneity of exposure histories of individuals imply that some caution should be taken with regards to these findings.

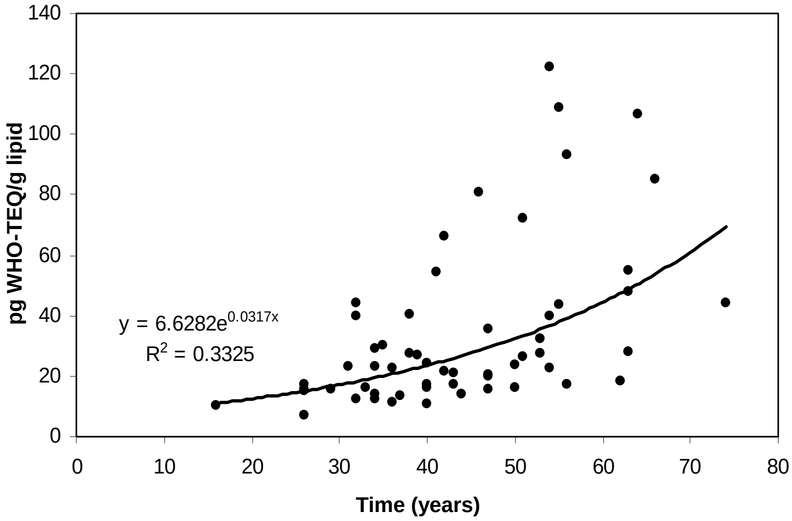


**Figure 1.**
Total TEQ values for dioxins (PCDD/Fs+PCBs) in serum of people with different exposure in relation to age. Data refer to both 1998 and 2007 monitoring and are fitted with a positive exponential relationship.

**Table 1.**
Relationship between TEQ and age: estimates of accumulation rates (k) and doubling time (years for the TEQ to double).

| | n | A pg TE/g lipid | k year-1 | $R^2$ | doubling time years |
|---|---|---|---|---|---|
| **PCDD/F** | 57 | 4.23 | 0.026 | 0.36 | 26.4 |
| **PCB** | 57 | 2.46 | 0.037 | 0.28 | 18.8 |
| **PCDD/F+PCB** | 57 | 6.63 | 0.032 | 0.33 | 21.9 |

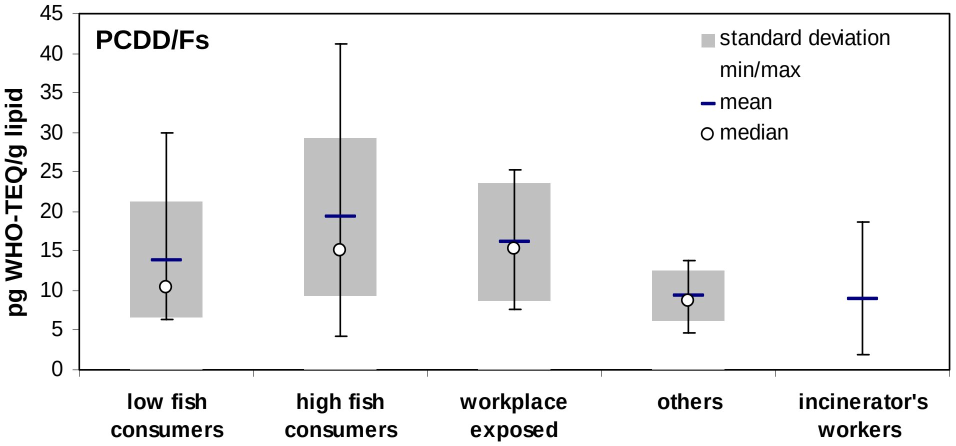


**Figure 2.** Comparison of PCDD/Fs total TEQ levels (WHO-TEFs) in human serum from the different data sets considered, according to known exposures.

Summary statistics regarding PCDD/Fs WHO-TEQ for data grouped according to the different potential exposure histories to dioxins are presented in Fig. 2. Data focussing on dietary exposures, referred to 41 Venetian volunteers (dataset A, 1998), show an average value of PCDD/Fs of 13.91 and 19.33 pg TEQ/g lipid for low (n=19) and high fish consumers (n=22), respectively. Recent data regarding a sample of 16 Italian volunteers (dataset B, 2007) show an average PCDD/Fs of 16.08 and 9.41 pg TEQ/g lipid for individuals subjected to occupational exposure (n=6) and for the others with not known concerning exposure life-histories (n=10), respectively. This last group has analogous average TEQ level found in serum of people (n=24) working in the Bolzano incinerator plant (9.00 pg TEQ/g lipid). However, the large dispersion of data and the relatively low number of samples do not allow for assessing strong statistical differences among groups. Summary statistics regarding PCBs-WHO TEQ are presented in Fig. 3. Dataset A evidences a significant difference between low and high fish consumers with averages of 9.30 and 30.68 pg TEQ/g lipid, respectively. Dataset B result in an average values of 22.00 and 6.77 pg TE/g lipid for occupational exposed and the others, respectively. Therefore, considering the two datasets, PCBs total TEQ values could be considered significantly different either between groups with documented different dietary habits (low and high fish consumers) or between groups distinguished on the basis of occupational or general exposure. Moreover, it is worth mentioning that values regarding total PCBs TEQ values for high fish consumers in Venetian population are comparable with the values of the group of people subjected to workplace exposure. However, caution should be taken when considering these preliminary evidences, because of the limited dimension of the samples (n=22 and n=6, for high fish consumers and workplace exposure, respectively). These results, anyway, highlight a clear need for further investigations.

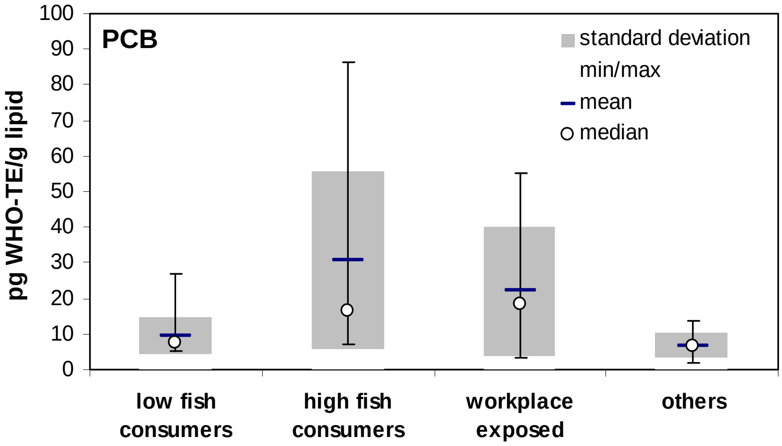


**Figure 3.** Comparison of PCBs total TEQ values (WHO-TEQ) in human serum from different data sets.

A first round comparison of dioxins fingerprints evidenced higher TCDF serum concentrations in high fish consumers than in low fish consumers, the former with levels comparable with those of people subjected to occupational exposure. However, the high concentrations of OCDD and the non-detectability of OCDF in the samples of dataset A (1998) might evidence a possible environmental contamination of the samples. Therefore the fingerprint analysis, that would have allowed only partial conclusion, is omitted here.

**Conclusions**

In this work, data of human serum PCDD/Fs and dioxin-like PCBs content referred to adult Italian men are presented. These data regard monitoring performed in 1998 and 2007and are the first of such kind in Italy a part from those related to the Seveso's accident[13]. Data from the two monitoring studies are aggregated into 4 different groups, which were identified on the basis of diverse potential exposure to dioxins: dietary habits distinguishing between high and low fish consumption are used for data collected in 1998; whereas occupational and general not-concerning exposures are invoked for grouping 2007 data. A clear positive exponential relationship between age and total dioxins TEQ levels is found and average doubling time ranged between 19 and 26 years, respectively for PCB and PCDD/Fs. Comparison of total PCDD/Fs TEQ values between 4 groups do not allow to recognize any statistically significant difference, even if a little enrichment could be linked to fish consumption and occupational exposures of Venetian volunteers. On the contrary, considering total PCBs TEQ, higher values are clearly associated to high fish consumers and workers of chemical plants of the Venice Lagoon. Notwithstanding low size of samples, these preliminary results are supporting concerns regarding human exposure dioxins and claim for further epidemiological studies in order to deep inside exposure levels for Italian population.

**Acknowledgements**

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