

# ENVIRONMENTAL LEVELS II

## POLYCHLORINATED DIBENZO-*P*-DIOXINS (PCDDs) AND FURANS (PCDFs) IN THE RIVER PO SEDIMENTS

Elena Fattore<sup>1</sup>, Luigi Viganò<sup>2</sup>, Giulio Mariani<sup>1</sup>, Andrea Guzzi<sup>1</sup>,  
Emilio Benfenati<sup>1</sup> and Roberto Fanelli<sup>1</sup>

<sup>1</sup> Department of Environmental Health Sciences, Mario Negri Institute for Pharmacological Research, via Eritrea 62, 20157 Milano, Italy.

<sup>2</sup> Water Research Institute CNR, 20047 Brugherio, Milano, Italy.

### Introduction

The River Po in northern Italy is the main Italian river, draining an area of 70,000 km<sup>2</sup> which is the most impacted by agricultural, industrial and urban activities.

Within a monitoring project to assess the environmental quality in the Po river<sup>1</sup>, polychlorinated dibenzo-*p*-dioxin (PCDD) and furans (PCDF) concentrations were determined in bottom sediments in summer and winter low-flow conditions. Sediments were collected just downstream from the confluence of the principal tributaries (Doria Riparia, Dora Baltea, Sesia, Tanaro, Ticino, Lambro, Adda, Oglio and Panaro) and in a reach of the upper course of the river (Monte Torino), located 50 km from the spring. This study represents the first investigation on PCDD and PCDF levels in sediments of the Po river.

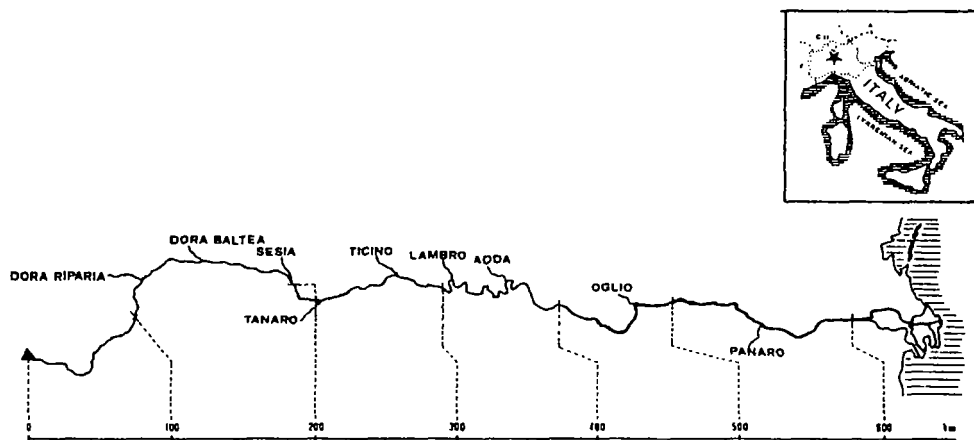


Figure 1. Watershed of the Po river with its main tributaries.

## Materials and Methods

The sediment collection started downstream from the completion of the mixing process between the main river and each tributary. A Ponar grab sampler was utilised to collect the samples of bottom river sediments. The samples were freeze-dried and the fraction  $< 0.63 \mu\text{m}$  was analysed. The analytical procedure was previously described<sup>2</sup>, briefly aliquots of 20 g were spiked with a mixture of fifteen 2,3,7,8-substituted congeners, soxhlet extracted with acetone/*n*-hexane 1/1 for 24 h, and purified by concentrated sulphuric acid on Extrelut column (Merck, Darmstadt, Germany) and by activated neutral alumina (Merck). Instrumental analysis was carried out with a DANI 6500 VG 70-250 high resolution gas chromatograph-mass spectrometer (HRGC-HRMS). The analysis of PCDD and PCDF isomers and homologue groups, was performed with a capillary column BPX 5 (SGE) 50 m  $\times$  0.22 mm, film thickness 0.25  $\mu\text{m}$ , and with a capillary column SP 2331 (Supelco) 60 m  $\times$  0.25 mm, film thickness 0.25  $\mu\text{m}$ . The GC-MS was employed in the selected ion recording (SIR) mode. Blank analysis was routinely performed and no contributions were detected.

## Results and Discussion

No substantial differences were found in the PCDD and PCDF concentrations between the summer and winter surveys. This observation is valid even considering that in the sediment samples collected in winter at Monte Torino and after the confluence of the Ticino river, the concentrations of PCDDs and PCDFs were too low to be detected under our experimental conditions. In fact, these results confirm both the low concentrations found in the corresponding summer samples and our knowledge<sup>1</sup> on the overall low levels of contamination of these two reaches of the River Po.

The mean values of the total PCDD and PCDF concentrations for the summer and winter surveys range from 121 to 736 ng/kg dry weight sediment (Fig. 2). Data on background levels of PCDD and PCDF concentrations in river sediments are very limited. Similar values to those detected in the present study, were found in sediments from the Red River in a non-industrial area in northern Vietnam<sup>3</sup>.

As expected, the lowest concentrations were detected in the Monte Torino sample (Fig. 2), that is in the sediments collected from the upper course of the river, before it receives important loads of contaminants. The highest concentrations were detected after the confluence with Doria Riparia and in the lower course of the river after the confluence with Lambro, Adda, Oglio and Panaro. Doria Riparia is exposed to high and direct load of effluents discharges, since it is the river passing through Torino, one of the biggest city in northern Italy.

## ENVIRONMENTAL LEVELS II

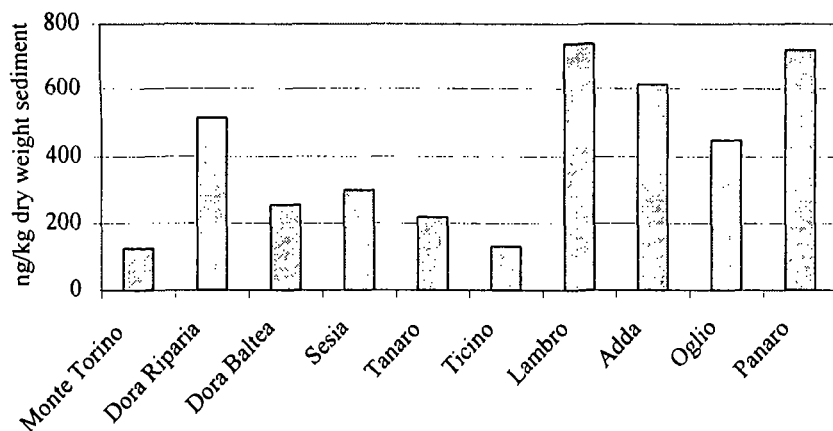
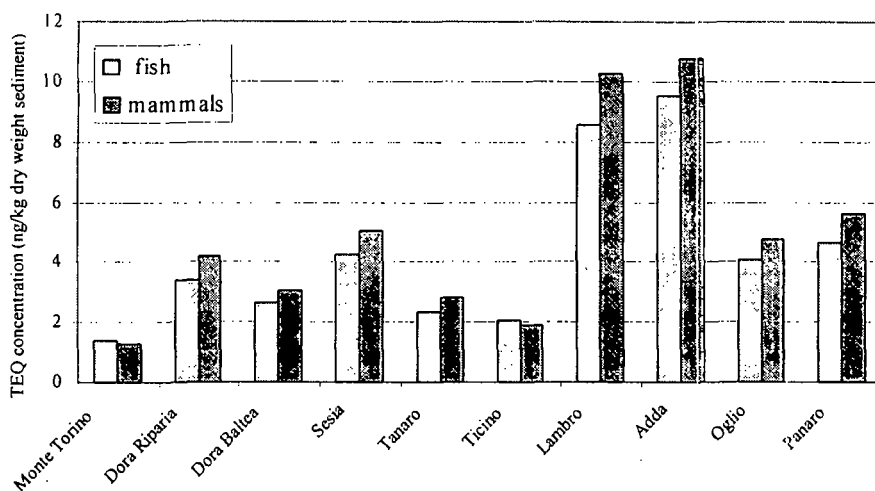


Fig. 2. Total PCCD and PCDF concentrations in sediment samples collected along the course of the Po river.

The higher concentrations in the sediment samples after the Lambro river were expected too, since this river drains the most heavily industrialised and densely inhabited basin of the entire Po watershed. Moreover in a recent investigation, Viganò and coworkers<sup>4</sup> found that the Lambro is an important source of polychlorinated biphenyls (PCBs) to the Po river. On the contrary the contamination loads from the Adda, Oglio and Panaro rivers was not expected, at least from our knowledge of their drain basins. At least for Adda and Oglio, one of the causes may be a dragging effect of the load of pollutants arising more upstream from the Lambro itself, as seems to be suggested by the spatial trend (Fig. 2).

Figure 3 shows the mean values of PCDD and PCDF concentrations reported as total Toxic Equivalent (TEQ) contents. For each sample, TEQ calculations were carried out using both the new toxic equivalency factors (TEF) recommended by WHO for fish and for mammals<sup>5</sup>. These concentrations are low and comparable to the background concentrations of sediments as reported in a recent EPA investigation<sup>6</sup>, with the exception of the sediments collected after the confluence of Lambro and Adda rivers (Fig. 3). At these two sites, the concentrations are from two to sevenfold higher than those downstream of the others tributaries. The partially different trend of the concentrations expressed as total PCDDs and PCDFs (Fig. 2) and as TEQ contents (Fig. 3) is mainly due to the higher contribution of the octachloro dibenzo-*p*-dioxin (OCDD) in the sediments collected after the confluence of Doria Riparia and after the confluence with Oglio and Panaro.

Fig. 3. TEQ concentrations, estimated by the TEF values for fish and mammals.



in sediment samples collected along the course of the Po river.

The PCDD and PCDF homologue profiles (Fig. 4) are characterised by OCDD which represents the most abundant congener, accounting from 40 to 60% of the sum of PCDDs and PCDFs. The heptachloro dibenzo-*p*-dioxins (HpCDDs) are the second most abundant homologue group in almost all the samples. When compared to the typical background homologue profile, arising from the atmospheric input, these samples show a slightly higher PCDD/PCDF ratio mostly due to lower concentration of OCDF and higher concentrations of OCDD. On the other hand, the predominance of the OCDD observed in the homologue profile of common sewage sludge<sup>7</sup>, seems to suggest that domestic wastewaters are the main source of PCDD and PCDF contamination for the sediments of the Po river.

# ENVIRONMENTAL LEVELS II

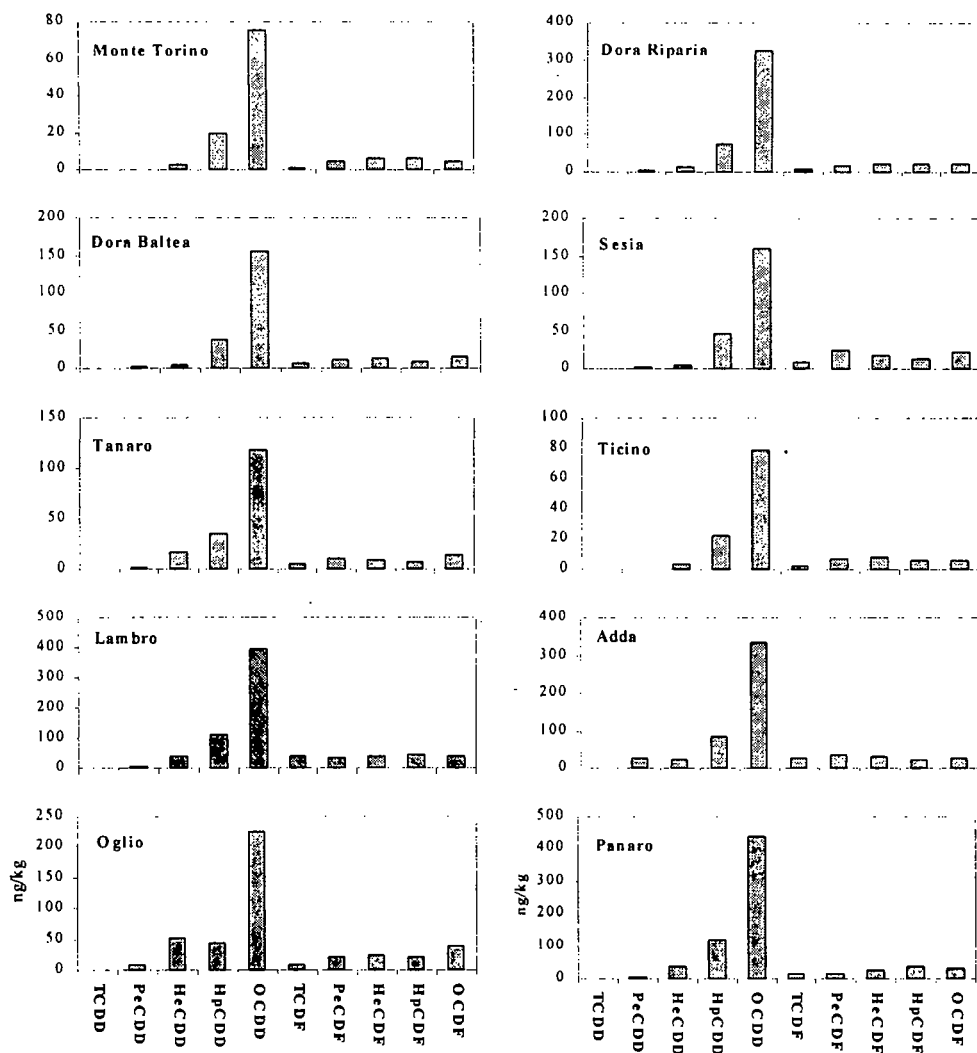


Fig. 4. PCCD and PCDF homologue concentrations in sediment samples collected along the course of the Po river.

## References

1. Viganò L. (2000) *Aquat. Toxicol.* 47, 191.
2. Fattore E., Benfenati E., Mariani G., Evers E. H. and Fanelli R. (1997) *Environ. Sci. Technol.* 31, 1777.
3. Schecter A., Eitzer B.D. and Hites R.A. (1989) *Chemosphere* 18, 831.
4. Viganò L., Arillo A., Aurigi S., Corsi I. and Focardi S. (2000) *Arch. Environ. Contam. Toxicol.* 38, 209.
5. Van den Berg M. *et al.* (1998) *Environ. Health. Perspect.* 106, 775.
6. USEPA Exposure and Health Assessment for 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) and related compounds (<http://www.epa.gov/ncea/pdfs/dioxin/dioxreass.htm>)
7. Broman D., Naf C., Rolff C. and Zebuhr Y. (1990) *Chemosphere* 21, 1213.

## ORGANOHALOGEN COMPOUNDS