

ENVIRONMENTAL LEVELS - POSTERS

POLYCHLOROBIPHENYLS (PCBs) IN SURFACE WATER OF THE VENICE LAGOON

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Introduction

In recent years, the Venice lagoon contamination has raised considerable concern due to the high toxicity of some persistent organic pollutants (POPs) detected there.^{1,2} These include PCBs and their related compounds, such as PCDDs and PCDFs, whose concentration levels in bottom sediments (and edible biota) of certain lagoon areas were found to be remarkably higher than those of background. These findings highlighted that an increased health risk might exist for residents, as particularly exposed to local fish food. In 1998, an additional three-year study was set out to improve the reliability of health risk estimates and identify possible risk reduction measures. Within the framework of this study,³ the levels of the microcontaminants of interest in the water body were investigated, also to assess possible relationships with their concentrations on suspended particulate as well as with the sedentary organisms exposed. Two lagoon zones were chosen, presumed to be under different environmental impacts; they were identified as *Alfa* and *Beta*. In this paper, the results of PCB assessment in the water bodies of such zones are presented.

Methods and Materials

For details on sampling, see Figure 1. In each subzone, three 5-L water samples were collected from three sites ("a", "b", and "c") by immersing an electric rotary pump (180 L/hour) down to approximately a 1-m depth, and pumping up the water. The three samplings were pooled in a stainless steel container for safe delivery to the analytical laboratory. Sampling was repeated several times in a month (Table 1). In the laboratory, water pools were filtered through fiberglass filters (0.7 μ m). PCBs in the aqueous phase were determined by continuous liquid-liquid extraction for 24 hours,⁴ using 10-L filtered water and 200 mL of a *n*-pentane-dichloromethane mixture (2:1, v/v). The extract was dried with anhydrous Na₂SO₄, and separated from it by pipetting out. Two 10-mL portions of *n*-hexane were used to wash out the residual Na₂SO₄; these portions were combined with the dry extract, and the mixture volume was reduced to 2 mL under nitrogen stream, for cleanup.⁵ Before extraction, the following ¹³C-labeled PCB congeners were added to the water phase as internal quantification standards: T₃CB[28], T₄CB[52], P₅CB[118], H₆CB[153], and H₇CB[180]. In addition, prior to extraction the (unlabeled) tracers T₃CB[30], T₄CB[77], P₅CB[126], H₆CB[157], and H₇CB[189] were added to the water phase at a level of 50 pg/L for accuracy and precision evaluation.

Cleanup was performed by adsorption chromatography by adding the 2-mL extract to a glass column (\varnothing = 6 mm) slurry-packed with 2 cm (top) of 60–100-mesh pesticide-grade Florisil RS and 1 cm (bottom) of 70–230-mesh alumina 60. Florisil and alumina, previously washed with

ENVIRONMENTAL LEVELS - POSTERS

n-hexane, were activated prior to use at 600 °C for 4 hours. PCBs were eluted with 30-mL *n*-hexane. The eluate was reduced to 100 µL under nitrogen stream and analyzed by HRGC-LRMS. The instrumental combination comprised a HP Mod. 6890 gas chromatograph and a HP Mod. 5973 mass selective detector. The GC unit was equipped with a HP-5 fused silica capillary column. Operating conditions were: injector temperature, 280 °C; transfer line temperature, 280 °C; oven temperature program, 70 °C (1 min), 10 °C/min to 150 °C, 10 min at 150 °C, 3 °C/min to 280 °C, 30 min at 280 °C; carrier gas (helium) flow, 0.8 mL/min; injection mode, pulsed splitless. Data were acquired in the electron impact mode (70 eV), using the selected ion technique. Each PCB congener was quantified with reference to a corresponding ¹³C-PCB. Crude concentration values were corrected with congener-specific instrumental response factors.

Four procedural blanks were distributed throughout the assessment sequence; procedural blank results were neglected in reporting sample concentrations. Accuracy and repeatability were as follows (mean and relative standard deviation): 50 pg/L and 10 % for T₃CB[30]; 58 pg/L and 13 % for T₄CB[77]; 61 pg/L and 9.0 % for P₅CB[126]; 49 pg/L and 6.0 % for H₆CB[157]; 49 pg/L and 12 % for H₇CB[189].









Results and Discussion

Figure 2 exhibits the total concentrations and profiles of dissolved PCBs in the eight samples collected during the sampling campaign of July 1998. From the figure, two distinct features may be preliminarily highlighted.

First, the sums of congeners (and to some extent, profiles as well) show a consistent difference according to their zone origin, that is *Alfa* or *Beta*. In fact, the values detected in Zone *Alfa*, presumed to be exposed to a more severe anthropogenic impact, are constantly higher for the entire sampling period. We recall here the specific exposures that were presumed to characterize Zones *Alfa* and *Beta*, as described in Figure 1. On the contrary, congener patterns appear to be fairly homogeneous in both zones. In fact, congeners with a lower chlorination degree prevail over the more chlorinated ones, in broad agreement with water solubilities.⁶ In particular, among the T₃- and T₄CBs, the congeners with IUPAC number 31+28, 52, and 47+48 seem to be consistently more prominent, a visual trait that characterizes the water phase.

In general, the above two features appear to reflect the effects of local anthropogenic impacts together with the physico-chemical properties of the compounds involved. Further experimental data expected from the ongoing work will allow a more thorough evaluation of the issue.

Table 1. Venice lagoon water sampling scheme.

SAMPLING DAY	SAMPLING POOLS			
	<i>Alfa 1</i>	<i>Alfa 2</i>	<i>Beta 1</i>	<i>Beta 2</i>
06/22/98				
06/23/98				
06/24/98				
06/29/98				
06/30/98				
07/01/98				
07/06/98				
07/07/98				
07/08/98				
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ENVIRONMENTAL LEVELS - POSTERS

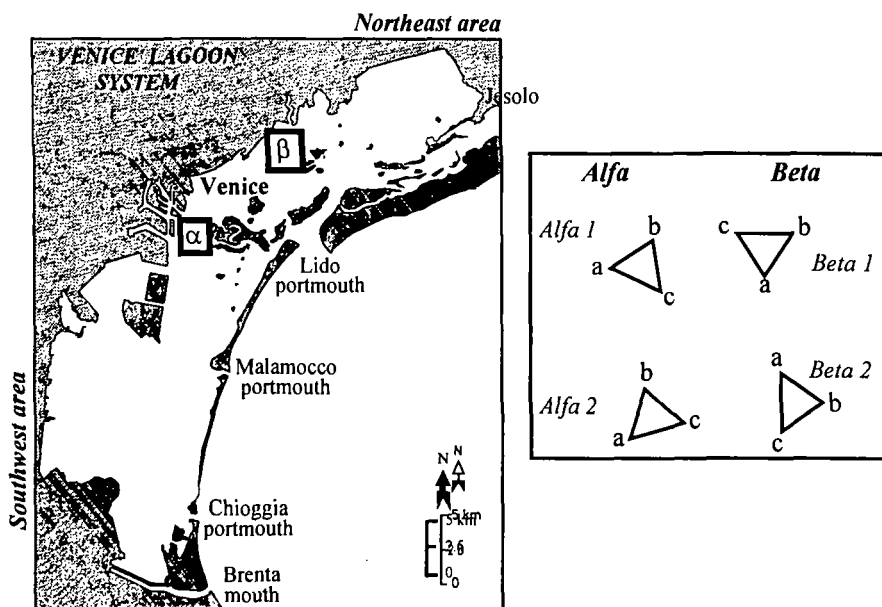


Figure 1. Sampling Zone *Alfa* was located in front of the Porto Marghera industrial area, regarded as heavily polluted, almost half-way between the latter and the City of Venice. Zone *Beta* was located near the Mazzorbo island, north-east of the City of Venice, in an area under agricultural impact. Each sampling zone was divided into two subzones: *Alfa 1* and 2, and *Beta 1* and 2.

Acknowledgments

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ENVIRONMENTAL LEVELS - POSTERS

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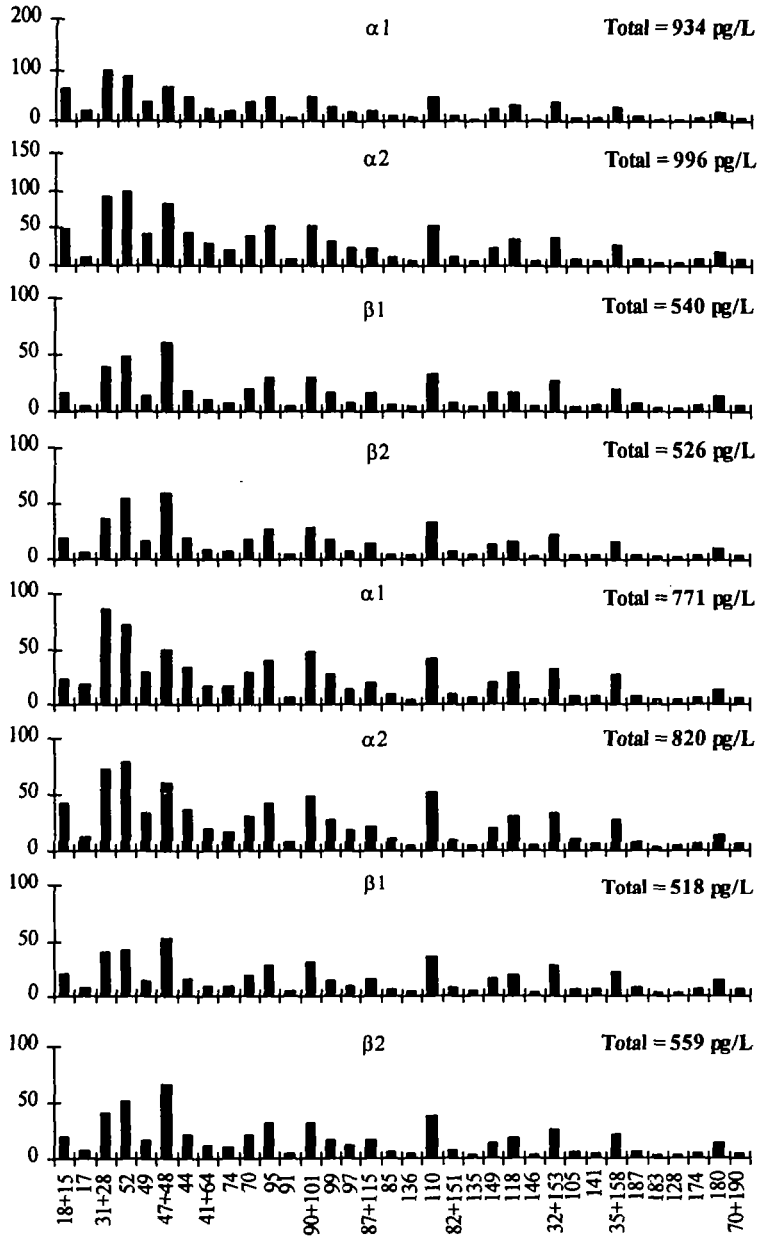


Figure 2. PCB congener profiles and total concentrations in Zone Alfa and Beta water samples.