PCB, PCDD and PCDF Contamination of Sediments from the Venice Lagoon

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1. Introduction

The 52-km-long 1-m-deep Venice lagoon lies in the northern Adriatic Sea. A large number of streams, outlets conveying industrial and urban sewage waters, and agricultural runoff discharge into the lagoon. The lagoon has limited water exchange with the open sea through three entrance channels. In addition, it is continuosly crossed by motorboats which both directly and indirectly contribute to the pollution load(1). These inputs represent important contamination sources to the sea water.

A project named Sistema Lagunare Veneziano (Venetian Lagoon System) was set up by the Italian National Research Council (CNR) to investigate, with the participation of many laboratories from Italian Universities and research Institutes, the lagoon pollution. The project includes the study of water, sediment and biota pollution and the determination of many organic and inorganic micropollutants and nutrients. The protocol of the study implies also QC/QA.

Sediments are generally considered a sort of archive of pollution of an area. So the study of their contamination and its evolution are important parameters to evaluate the pollution of the associated ecosystem.

2. Materials and methos

Samples were collected by a steel dredge in the summer of 1992 by an oceanographic ship. Table1summarizes the information on sampling.

Table 1. Description of sampling sites.

Sample code	Site name	Site description	pollution sources	Depth
Site1	Porto Marghera	industrial area	chemical and oil refining plants	1 m
Site 2	Mouth of River Dese	agricultural area	inputs from urban and industrial areas upsteams	1-2 m
Site 3	Canal Grande	Downtown Venice	urban sewages;exhaust from motor boats	6-7 m
Site 4	Sacca Sessola	bay between sea channels	local marine traffic	1-2 m
Site 5	Chioggia Basin	fishing harbour	local marine traffic	1-2 m
Site 6	Offshore platform	Adriatic sea	long range transport	15 m

The sampling locations were thought to be representative of different kinds of pollution. Site 1 is located in the industrial area of Porto Marghera. Site 2 is at the mouth of River Dese, the most important river in the northern part of the lagoon: the river flows through vast agricultural areas and industrial towns (50.000-200.000 inhabitants). Site 3 is located in downtown Venice (Canal Grande). Site 4 corresponds to an area of intensive commercial traffic (Sacca Sessola). Site 5 corresponds to the fishing harbour of Chioggia. Site 6 is situated in the open sea, near a survey platform (1).

After sampling, sediment samples were kept at -20 °C.The following assays were carried out on these samples:

i) PCBs, PCDDs and PCDFs;

ii) PAHs and mutagenicity.

In the present paper only data relative to organochlorine compounds will be presented.

Before the extration the samples were spiked with a mixture of the following wholly^{13}C labeled standards: 2,3,7,8 T_4CDD; 1,2,3,7,8 P_5CDD; 1,2,3,7,8,9 H_6CDD; 1,2,3,4,6,7,8 H_7CDD; O_8CDD; 2,3,7,8 T_4CDF; 2,3,4,7,8 P_5CDF; 1,2,3,4,7,8 H_6CDF; 1,2,3,4,6,7,8 H_7CDF; 2,4,4'-T_3CB; 2,2',5,5'-T_4CB; 3,3',4,4'-T_4CB; 2,2',4,5,5'- P_5CB; 3,3',4,4',5- P_5CB; 2,2',4,4',5,5'-H_6CB; 3,3',4,4',5,5'- H_6CB; 2,2',3,3',5,5',6- H_7CB.

Extraction was performed with a *n*-hexane-acetone (1:1) mixture (200 ml) with a mechanical aid (2,3).The operation was repeated several times. All the extracted fractions were combined together to yield a single pool. Evaporation of extracted fractions was carried out by a rotary evaporator.

The first cleanup was a liquid partition with water and *n*-hexane in a separatory funnel. This treatment was repeated several times. In the end all *n*-hexane fractions were pooled together. The pool of hexane extracts was dehydrated overnight with anidrous sodium sulfate.

The dry pool was percolated over Extrelut impregnated with 96% sulfuric acid (column dimension: 2 cm i .d. by 13 cm heigt) (3,4).

After the acid treatment the hexane phase was evaporated to <l0 mL and trasferred to a 10 mL test tube and further concentrated or made up whith *n*-hexane to a final 3 mL volume. Then a few drops of mercury were added and the tube was shaken vigorously for 45 minutes. Mercury treatament was required to remove dissolved elemental sulfur extracted from the matrix (5-7).

Table 2. Total concentrations of the three families of organochlorine compounds and Toxicity Equivalents (I-TEFs) of PCDDs+PCDFs. Only 2,3,7,8- substiyuted PCDDs and PCDFs were determined.

	SITE 1	SITE 2	SITE 3	SITE 4	SITE 5	SITE 6
Σ PCB (ng/g)	16	6	294	10	6	6
ΣPCDD (pg/g)	74	19	319	26	34	0.7*
Σ PCDF (pg/g)	413	18	240	61	28	0.6*
ppt TE tot	7.8	0.7	15.0	1.9	1.3	

*Sum of detection limits

An additional 96% sulfuric acid treatament (multilayer chromatographic column) followed (2,3). Finally the organic matrix was eluted over an activated neutral alumina column to separate PCBs and other background compounds (Fraction I) from PCDDs and PCDFs (Fraction 2)(2-4).

The two fractions were quantitated separately by HRGC-MS: PCBs on a HP5989A instrument; PCDDs and PCDFs on a VG Autospec high resolution mass spectrometer (R=10,000). Both the instrumens were equipped with on column injectors and a HP Ultra 2 capillary gas cromatographic column (50-m-long 0.32 mm-i.d.). Details on organochlorine compounds determination are described in previuos papers(8,9)

3. Results

In Table 2 the overall concentrations of the three families of organochlorine compounds are shown. The detailed description of the congener patterns of the single sites will be reported in an extended paper. In many cases most of the chlorinated dioxins (T_4CDD, P_5CDDs, H_6CDDs) were not determinable; on several samples, also tetra to hexa PCDFs were not determinable. Only in the sample from downtown Venice all seventeen 2,3,7,8-substituted PCDD and PCDF congeners were determined. By contrast, none of them was determinable in sediment from site 6 (open-sea platform). Between these two extremes, all other sediments show intermediate contamination levels. PCB contamination levels follow a similar trend.

4. Discussion

The central area of Venice is by far the most polluted among the sites considered, followed by the industrial site of Porto Marghera. In the latter site, the high level of PCDFs seems to indicate a specific industrial source; the particularly high level of 1,2,3,4,7,8-H6CDF, can possibly be related to chloroalkali plants(10).

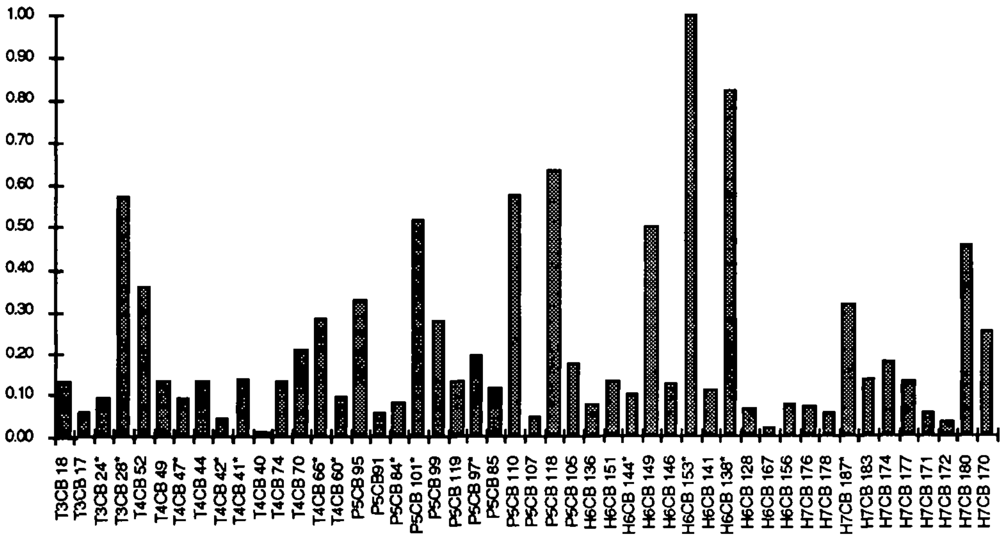

Figure 1. Pattern of PCB congener distribution; mean of all samples.

In figure 1 the PCB congener mean pattern is shown: 48 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, H6CB 153, made equal to 1. PCB patterns from the variuos sites do not show great differences between each other, with the main exception of T3CBs, whose relative intensity varies sensibly from site to site.
In figure 1, PCB 77, altough present in the sediments, is not represented, because in the allumina column, it elutes with the PCDDs and PCDFs. Its determination is still in progress.

5. References

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