

PCDD/Fs and PCBs in Sediment Samples from the Venice Lagoon

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Introduction

Sediments from certain areas of the Venice Lagoon have recently been reported to contain high levels of PCDD/Fs and PCBs, while other parts of the Lagoon remain relatively free of contamination. In addition to the implications this has had on the ecology of the Lagoon, the ability for shellfish to accumulate these toxicants has raised concern about the potential human dietary exposure in this region. The farming of shellfish is a major industry in the Lagoon and provides for a high consumption rate in the region. Previous studies have examined sediments from particular areas. In this paper we report PCDD/F and PCB concentrations in 68 sediment samples taken from throughout the Lagoon to provide an overview of the extent of contamination of the entire area. At fourteen of the sampling sites a two meter core was taken to establish to what depth the contamination is confined.

Materials and Methods

Surface sediment to a depth of 15cm was collected from 54 sites. 2m cores were collected from 14 sites and divided into four sections: 0-15cm, 15-50cm, 50-100cm and 100-200cm. Samples were well mixed and a portion separated for transport, frozen, to Lancaster. Subsamples were mixed (1:2) with anhydrous sodium sulphate, spiked with 20 ¹³C₁₂-labelled PCDD/F congeners and 9 ¹³C₁₂-labelled PCB congeners, and soxhlet extracted with toluene for 16 hours. The extract was cleaned up by adsorption chromatography with acid treated, base treated and activated silica gel, gel permeation chromatography (S-X2 Biobeads) and sulphur removal with copper. Alumina B Super-1 (ICN Biomedicals, Eschwege, Germany) was used to fractionate the cleaned extract, separating PCDD/Fs from Non-ortho PCBs (#77, #126 and #169) from Orthochlorinated PCBs. PCDD/Fs were quantified by HRGC/HRMS (HP 6890/Micromass Autospec Ultima) using HP5-ms and SP2331 capillary columns. Non-ortho PCBs were quantified by HRGC/HRMS using a HP5-ms column, orthochlorinated PCBs were quantified by HRGC/LRMS (Fisons GC8000/Fisons MD800) using an Ultra 2 column. A laboratory blank and a standard reference sediment were run with each batch of ten samples. Blanks were quantified and used to calculate limits of detection as the mean plus 3 times the standard deviation.

Results

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ΣPCDD/F ranged between <1 - 40500pg/g dry weight for surface sediments and <1 - 44000pg/g dry weight for subsurface cores. ΣPCBs ranged <2 - 869ng/g dry weight and <2 - 1701ng/g dry weight respectively. TEQ values ranged between <0.4 - 465pg/g dw, with PCDD/Fs generally contributing ca 80%, coplanar PCBs 15% and orthochlorinated PCBs 5% of the total. The samples were from most parts of the Lagoon so a PCDD/Fs contamination map (Figure 1) has been prepared. On account of the huge range of levels encountered, log(10) values have been plotted in Figure 1. so that concentrations rise exponentially, not geometrically, through the colour scheme. Plotting PCBs in this way gave a very similar distribution. Variation of contamination with depth differed between the fourteen sediment cores. In some of the more polluted cores, the highest concentrations of PCB/DD/DFs were encountered in the 50-100cm section, including the highest value of all those analysed. This could be an artifact of dredging or mechanical mixing of layers, or it could represent historical trends. In the less contaminated cores the concentrations dropped to around detection limits in the deeper sections without a subsurface maximum.

Discussion

As has been reported previously⁽¹⁻⁴⁾, most parts of the Lagoon were found to be relatively clean. 66% of surface sediments in this study had ΣPCDD/F concentrations <250pg/g dry weight which is comparable to levels seen in "pristine" or "background" lake sediments^(5,6). Similarly, ΣPCB was <10ng/g for 70% of the surface samples. Median concentrations were 140pg/g and 6ng/g respectively. Elevated concentrations were identified in the vicinities of Porto Marghera (a major chemical industrial zone), the Malamocco canal (the main watercourse and shipping route connecting the Port to the Sea), Fusina (site of a power station, an incinerator and a water treatment plant) and around the outflows of the Dese, and Brenta rivers.

Table 1.

	TEQ ng/g dw	TEQ @ 10% Organic Matter
Marghera industrial zone (This study)	10-500	10-1010
Hamburg Harbour (Germany) ⁽⁷⁾	25-175	
Pulp mill Outflow (British Columbia) ⁽⁸⁾	1-900	
Rhine Estuary (Netherlands) ⁽⁹⁾	45 (mean)	
Chemie Harbour (Netherlands) ⁽¹⁰⁾		1096 (mean)

PCDD/F and PCB results from previous studies of Venice Lagoon are in broad agreement with those reported here and generally fit well into Figure 1. Whereas this study had no samples taken from within the City of Venice, the results of both Fattore *et al.*⁽⁶⁾ and Di Domenico *et al.*⁽³⁾ indicate that this area would be an additional area of elevated concentrations of both analyte families, similar to those of the two river outflows. The highest levels of both sets of compounds found in this study were in the industrial area of Marghera. Indeed concentrations in sediments from this area were an order of magnitude higher than any of the other areas mentioned above - even samples from the Marghera Harbour^(1,4). The extent of pollution here is comparable to various highly polluted regions around the world: Principal Components Analysis of the data showed one cluster of samples with high contributions of heavily chlorinated PCDFs and another cluster having high contributions of heavily chlorinated PCDDs, similar to the findings of Jimenez

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et al.⁽¹⁾ and Fattore *et al.*⁽⁴⁾. Samples from the Marghera region exhibited the former pattern, whilst samples from the Dese outflow in the north and the Brenta in the south had patterns with higher OCDD contributions. The homologue pattern of sediments all along the Malamocco Canal matches exactly that of sediments from the Marghera industrial zone, which confirms that the elevated levels of PCDD/Fs found in the canal are due to migration of sediments/pollutants from Marghera. Sediments from the remainder of the Lagoon showed a pattern somewhere between the two distinct profiles. This does not necessarily mean that the background contamination is a product of these two sources - indeed this seems unlikely as i) there was no apparent gradation of the pattern based on proximity to one or other of the pattern sources, and ii) except down the Malamocco Canal, there does not appear to be evidence of widespread dispersion of the contamination. If this had been the case, the background pattern would be expected to be more closely related to the Marghera profile than that of the river outflows on account of the relative degree of contamination of the two genera. The elevated samples at Fusina showed individual patterns and suggest specific local sources to these sites.

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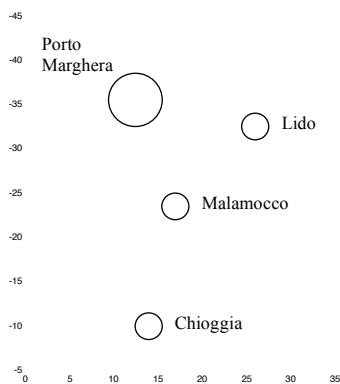


Figure 1.
PCDD/F concentration map
of Venice Lagoon.

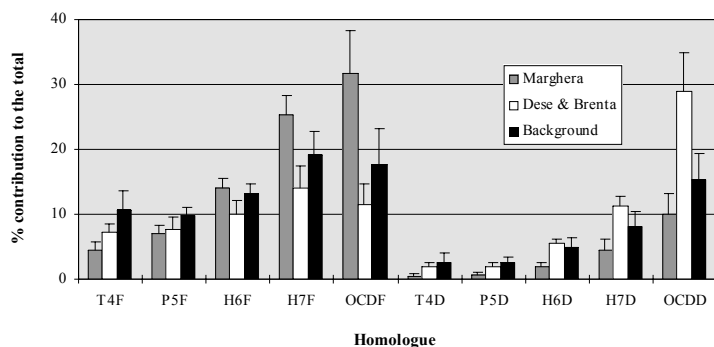
Values are $\log(10)$
 Σ PCDD/F concentrations
measured in 68 sediment
samples.

The map was generated by
interpolation of these data

Figure 2.

PCDD/F homologue profiles in sediments from three generic locations of the Lagoon

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