CRABS AND SEDIMENT FROM THE VENICE AND ORBETELLO LAGOON

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Introduction

The presence of PCDDs, PCDFs and PCNs in sediments of waterways in industrialized and heavily populated areas is an environmental problem that has received considerable attention in recent years. There is growing evidence that these compounds are extremely harmful to marine and freshwater ecosystems, especially when they bioaccumulate through aquatic foodwebs. PCDDs and PCDFs are formed as a byproduct of various chemical and combustion processes and enter the aquatic environment from the atmosphere and as direct discharges from industrial sources, sewage treatment plants, and storm drains. On the other hand, there are three main sources of PCNs: a) the use of technical PCN products manufactured in different countries under various trade-names such as Halowax, Seekay Wax and Nibren Wax; b) the use of commercial PCB products, such as Aroclor or Clophen, which have, at the ppm-level, PCNs as by-products; and, c) the formation during high temperature processes.

The purpose of this study was to evaluate the contamination caused by PCDDs, PCDFs and PCNs in two polluted Mediterranean lagoons. Surface sediment and crab samples from Venice and Orbetello lagoons were analysed. The Venice lagoon has a surface area of 550 Km^2 and communicates with the Adriatic sea, in northeast Italy. The water exchange with the Adriatic sea occurs through three entrance channels, dividing the lagoon into three basins: Lido, Malamocco and Chioggia. Streams and outlets discharge industrial effluent, urban sewage and agricultural runoff into the lagoon, which has a limited water exchange with the open sea. Heavy motorboat traffic on the lagoon contributes directly and indirectly to the contaminant load. The Orbetello lagoon is located between the Tuscany coast and Monte Argentario, is trapeze-shaped and has a surface area of 2700 ha.The lagoon is divided into two main basins: Ponente and Levante. The water exchange with the Mediterranean sea is through two channels in the Ponente lagoon and one channel in the Levante lagoon.

Materials and Methods

Sample sites

Sediments

In 1995, samples were taken from surface sediments (upper 5 cm) with a stainless steel box at different sites, characterised by different types of contamination. For the Venice study, five sites were selected: "Giudeca Island" (station SVA), an area with heavy pollution due to motorboat traffic and the presence of untreated sewage from the city of Venice; "Pellestrina" (station SVB), a zone selected as a control site, far from industrial areas, with a moderate water exchange; "Chioggia harbour" (station SVC), an area of the lagoon affected by considerable harbour activity, with an ample water exchange; "Porto Marghera" (station SVD), an area with a high industrial impact due to chemical and oil refining plants, with a slow water exchange; "Dese River" (station SVE), a zone with a slow water exchange, affected by an agricultural impact. For the Orbetello study, four sites were selected:"Santa Liberata" (station SOA), a channel connecting lagoon and sea; "Orbetello" (station SOC), a sewage treatment plant using chlorine at Orbetello, with a moderate water exchange; a fish farm (station SOD); and "Albegua River" (station SOE), a zone selected as a control site.

Crabs

In the Venice lagoon, male specimens of *Carcinus aestuarii* were collected in the same sites as those from which sediments were taken. The crabs were sacrificed, and their tissues stored at –80ºC until analysis. In the Orbetello lagoon 36 male specimens of *Carcinus aestuarii* were obtained from station A, which was selected as the control site. Three different groups were made taking 12 individuals per group which were caged: one group was kept at location A and the other two groups were transferred to locations B and C where they were maintained for a period of 15 days.

Extraction and clean-up

The samples were manually ground, oven dried (50ºC) and sieved to 0.25 µm before extraction. Twenty g dry weight (d.w.) sediment samples were extracted in a Soxhlet apparatus for 24h. After extraction, the clean-up of the extracts was performed via a 2-stage open column chromatographic procedure: modified silica and Florisil. The PCNs elute together with PCDDs and PCDFs.
For crab samples, extraction and clean-up were performed as described in detail in reference [1].

Instrumental Analysis

Purified PCDD, PCDF and PCN extracts were analysed by HRGC/HRMS. Analyses were performed on a Fisons 8060 gas chromatograph fitted to a VG AutoSpec-Ultima (VG Instruments, Manchester, UK) mass spectrometer, operating in the electron impact ionization (electron energy 38 eV) at 10000 of resolving power. A DB-5 fused-silica column (J&W Scientific, Folsom, CA, USA) capillary column (60m x 0.25 mm I.D., 0.25 µm film thickness) was used with helium as the carrier gas at a pressure of 175 Kpa. For PCDD and PCDF determinations, the temperature programme was from 140ºC (held for 1 min.) to 200ºC (held isothermally for 1 min.) at 20ºC/min., and then from 200ºC to 300ºC (maintained for 20 min.) at 3ºC/min. For PCN determinations, the temperature programme was from 60ºC (held for 1 min.) to 150ºC (held isothermally for 1 min.) at 20ºC/min., and then from 150ºC to 285ºC (maintained for 20 min.) at 3ºC/min.

Results and Discussion

PCDD and PCDF results

Levels of 2378-substituted PCDD and PCDF congeners and calculated I-TEQs in all sediment samples studied are shown in table 1. All 2378-substituted PCDD/Fs were detected in almost all sediments with differences between sampling sites. For the Venice study, total I-TEQ values ranged from 2.31 to 34.85 pg/g, being site SVD the most contaminated, followed by SVA, SVC, SVB and SVE. PCDDs constituted between 8 and 20% of the total I-TEQ, while PCDFs contributed at least 80%. Relatively high levels were found in sediment from the Porto Marghera harbour (34.85), especially when this value is compared with the quality objective of 20 pg I-TEQ/g [2]. For the Orbetello study, total I-TEQ values ranged from 0.21 to 4.11 pg/g, being site SOC the most contaminated, followed by SOA, SOE and SOD. Total PCDDs were always higher than total PCDFs in contrast with the tendency found in sediments from Venice [3].

For crab samples from the Venice lagoon, total I-TEQs ranged from 1.10 pg/g to 4.24 pg/g. The general trend in PCDD and PCDF levels found in sediments was also observed in crabs, with total PCDFs being higher than total PCDDs, but the congener patterns were different from those of sediments and varied between sites. For crab samples from the Orbetello lagoon, total I-TEQs ranged from 1.12 pg/g to 4.28 pg/g. The general trend in PCDD and PCDF levels found in sediments was different in crabs, total PCDDs and PCDFs being almost equal in the three station studied.

PCN results

PCNs were detected in all the sediments studied. The concentrations of the mono- through octa-CN in the different samples analysed are given in table 2. As for the Venice study, site SVD (Porto Marghera harbour), part of the Venice lagoon which is characterised by high industrial impact, exhibited the highest levels followed by SVA>SVC□SVE>SVB. The lowest concentrations, as expected, were in sample SVB, which was collected as a site control. Total PCN levels ranged from 34.16 pg/g detected at site SVB to 956.63 pg/g at site SVD. As regards the Orbetello study, site SOC, a sewage treatment plant, presented the highest levels followed by SOE□SOD□SOA. Total PCN levels ranged from 57.96 pg/g detected at site SOA to 1515.36 pg/g at site SOC [4].

Correlation within PCDD and PCN data

When comparing the levels of PCNs with those of PCDDs and PCDFs, some features should be pointed out. The samples with the highest levels of PCDDs and PCDFs also present the highest levels of PCNs. Thus, in the Venice study, the SVD sample showed the highest PCDD/F contamination with an I-TEQ of 34.85 pg/g. The PCN results also showed the highest concentration, with a value of 956.63 pg/g. As for the Orbetello investigation, the SOC sample showed the highest contamination of PCDDs/Fs and PCNs, with levels of 4.11 pg I-TEQ/g and 1515.36 pg/g, respectively. The decreasing order SVD>SVA>SVC□SVE>SVB and SOC>SOE□SOD□SOA for the PCN determinations resembled that obtained for the PCDD and PCDF analyses.

Some PCN congeners are highly active as EROD and AHH inducers and as a result have an assigned TEF [5]. Nevertheless, other potentially very toxic PCN congeners do not have an

assigned TEF. For this reason, and as an approximation, we evaluated our findings in terms of dioxin toxicity equivalents (TEQs). PCNs could contribute to the total TEQ, though not significantly. In the Venice samples, the contribution of PCNs to the total TEQ ranged from 0.7 to 1.6%, and from 1.8 to 6.2% for the Orbetello samples.

Table 1 PCDD and PCDF levels (pg/g) in sediments from the Orbetello and Venice lagoons.

	SVA	SVB	SVC	SVD	SVE	SOA	SOC	SOD	SOE
2378-TCDD	0.08	0.07	0.13	0.40	0.06	0.02	N.D.	0.02	N.Q.
12378-	0.30	N.Q.	0.35	1.71	0.20	0.10	N.D.	N.Q.	N.Q.
PeCDD	0.45	0.22	0.30	2.43	0.29	0.09	1.27	0.06	0.18
123478-	0.63	0.38	0.99	3.35	0.51	0.08	2.41	0.05	0.11
HxCDD	0.88	0.61	1.01	4.72	0.69	0.10	2.45	0.06	0.28
123678-	6.67	4.87	15.03	43.57	5.75	0.74	47.72	0.43	1.99
HxCDD	43.96	25.31	65.37	155.2	27.91	3.77	335.2	3.03	14.97
123789-				0			7		
HxCDD	4.71	2.72	3.85		2.09	0.52		0.30	0.32
1234678-	1.69	0.91	1.28	20.89	0.75	0.13	5.24	0.15	0.21
HpCDD	2.97	1.34	2.12	10.43	1.43	0.23	1.51	0.10	0.17
OCDD	12.97	5.08	7.16	15.00	4.20	0.42	1.89	0.25	0.41
	4.88	1.94	2.69	105.2	1.65	0.23	5.18	0.16	0.21
2378-TCDF	3.75	1.91	2.62	8	1.71	0.24	1.94	0.17	0.24
12378-	0.56	0.32	0.47	34.75	0.28	0.16	2.64	0.16	0.17
PeCDF	43.80	15.82	22.69	27.93	14.29	0.71	N.Q.	0.53	1.29
23478-	5.02	2.00	2.14	3.98	1.49	0.14	16.66	0.10	N.Q.
PeCDF	57.05	19.54	17.64	367.3	15.59	0.81	N.Q.	0.61	4.00
123478-				5			N.Q.		
HxCDF	5.34	2.37	3.82	48.86	2.31	0.40		0.21	0.35
123678-				484.6			4.11		
HxCDF				2					
234678-									
HxCDF				34.85					
123789-									
HxCDF									
1234678-									
HpCDF									
1234789-									
HpCDF									
OCDF									
Total I-TEQ									

N.D. = Not Detected N.Q. = Not Quantified ($R_{s/n} < 3$)

Table 2 PCN levels (pg/g) in sediments from the Orbetello and Venice lagoons.

	Mono	Di	Tri	Tetra	Penta	Hexa	Hepta	Octa	Total
SVA	1.84	3.19	28.82	89.66	44.36	17.20	4.31	1.92	191.30
SVB	0.82	N.Q.	3.23	16.30	7.01	4.24	1.62	0.95	34.16
SVC	10.51	16.56	14.96	59.40	22.40	7.46	2.02	1.11	134.42
SVD	43.05	148.2	105.4	337.6	180.2	107.9	24.75	9.31	956.63
SVE	6.18	7	4	3	5	3	3.18	2.02	132.08
		2.45	14.44	63.15	31.20	9.45			
SOA	5.09						3.19	1.78	57.96
SOC	29.26	N.Q.	4.12	26.92	11.23	5.63	7.30	N.Q.	1515.3
SOD	5.77	4.88	186.5	791.7	427.8	67.78	0.36	1.04	6
SOE	4.83	N.Q.	8	3	2	0.90	0.93	1.06	66.82
		N.Q.	17.73	36.82	4.21	2.13			76.12
			15.39	46.11	5.68				

N.Q. = Not Quantified ($R_{s/n} < 3$)

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