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PCDDs and PCDFs in crabs and sediments from Venice Lagoon (Italy)

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Abstract

2,3,7,8 chlorinated PCDDs and PCDFs were determined in crab and sediment samples taken from different locations in Venice Lagoon (Italy) characterised by different types of contamination. Differences in PCDD/F levels were found depending on the sampling site. Major levels were found in Porto Marghera harbour characterised by a high industrial impact.

Introduction

Polychlorinated dibenzo-p-dioxins (PCDDs), and dibenzofurans (PCDFs) have been detected in a wide range of environmental matrices. They are known to be highly toxic and persistent due to their lipophilic properties⁽¹⁾. The presence of PCDDs, PCDFs and PCBs in sediments of waterways located in industrialized and heavily populated areas, is an environmental problem that has received considerable attention in recent years⁽²⁾. There is growing evidence that these compounds are extremely harmful to marine and freshwater ecosystems, especially when they bioaccumulate through aquatic foodwebs⁽³⁾.

This study was focused on the pollution in the Venice Lagoon (Italy) which lies in the norther Adriatic Sea. A large number of streams, outlets conveying industrial and urban sewage waters, and agricultural runoff discharge into the lagoon. The lagoon has a limited water exchange with the open sea through three entrance channels. In addition, it is continuously crossed by motorboats which both directly and indirectly contribute to the pollution load. These inputs represent important contamination sources to the sea water.

Sediments and crabs were sampled in five different sites in Venice Lagoon characterised by different types of contamination. Contamination studies in sediments are generally considered to be very appropriated for the studies of the pollution of an area and important parameters to evaluate the pollution of the associated ecosystem⁽⁴⁾.

The crab *Carcinus aestuarii* was used as bioindicator organism for the coastal marine environment and application of a multi-trial biomarker approach for ecological risk assessment. There are several reasons why invertebrates are preferable in this ecotoxicological area⁽⁵⁾. For example invertebrates constitute 95% of all animal species⁽⁶⁾. They are major components of all ecosystems, and invertebrate populations are often numerous, so that samples can be taken for analysis without significantly affecting population dynamics. In ecotoxicology studies, invertebrates have an advantage over the fish in that they remain in a confined area.

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Material and Methods

Sampling

Sediments.

In September 1995, samples were taken from surface sediments (upper 5 cm) with a stainless steel box in 5 different sites in Venice Lagoon characterised by different types of contamination. Table 1 summarizes the information concerning to sampling sites. Freshwater sediments were not sieved as nearly all material in sedimentation areas belongs to the <63 μ fraction.

Crabs

Male specimens of *Carcinus aestuarii* were collected in the same sites where sediments were taken. The crabs were sacrificed and tissues were maintained at -80°C until analysis.

Table 1. Description of sampling sites selected in Venice Lagoon (Italy).

<u>Code</u>	<u>Site name</u>	<u>Site description/Pollution sources</u>
Site A	Giudeca Island	Urban impact
Site B	Pellestrina	Control site
Site C	Chioggia harbour	High harbour activity
Site D	Porto Marghera	Industrial impact/chemical and oil refining plants
Site E	Dese River	Agricultural impact

Analytical determination

- Extraction and clean up

Crabs

Extraction and clean up followed a method previously described in detail in previous work ⁽⁷⁾. Basically this comprises low pressure chromatography on neutral and base-modified silica gel, activated carbon dispersed on glass fibers, silica gel impregnated with sulfuric acid, and Florisil. Three fractions were eluted from the carbon column for each sample. These contained ortho-substituted PCBs, non-ortho-substituted PCBs and PCDD/Fs respectively.

Prior to the initial extraction of samples, a mixture of ¹³C₁₂ PCDD/Fs and non-ortho substituted PCBs internal standards, was added containing one isomer for each 2,3,7,8-substituted congener with the exception of 1,2,3,7,8,9-HpCDD and OCDF. Amounts between 3 and 5 grams of muscle were used for analysis. For each location pool samples were made using a number of five individuals.

Sediments

PCDD/Fs analysis were performed on approximately 20 g of sediments dried and spiked with a mixture of 15 [¹³C₁₂] which were Soxhlet extracted with toluene for a period of minimum 24 hours. Clean up followed a method previously described in detail ⁽⁸⁾.

- Quantification

Resolution and quantification of PCDDs, PCDFs and co-planar PCBs were performed by HRGC-HRMS using a VG AutoSpec Ultima (VG Analytical, Manchester, U.K.) coupled to a Fisons Series 8000 (8060) Gas Chromatograph. A fused silica capillary DB-5 column (60m, 0.25 mm i.d., 0.25 μ m film thickness, J&W Scientific, U.S.A.) was used using helium as carrier gas at a column head pressure of 175 Kpa. A minimum resolution of 10,000 was used when operating with the HRMS instrument.

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Results and Discussion

Table 2 presents congener-specific results of PCDD/Fs and calculated I-TEQs^(9,10) in all the sediments analysed. Only 2,3,7,8-substituted congeners are reported due to their toxicological interest. Note that total values quoted have been calculated assuming that all values less than the limit of detection (LOD) are equal to the half of the LOD.

In all sediments all 2,3,7,8-substituted PCDD/PCDF were detected. Data indicates differences in the levels of pollution depending on the sampling site. Location D (Porto Marghera harbour) was found to exhibit the highest levels followed by A>C>B=E. Total PCDD and PCDF levels ranged from 78.89 ppt detected in site E to 1330.47 ppt detected in location D.

Table 2. PCDD and PCDF levels in sediments from five locations sampled (pg/g dry weight).

Isomer	A	B	C	D	E
2378-TCDD	0.08	0.07	0.13	0.40	0.06
12378-PeCDD	0.30	**0.05	0.35	1.71	0.20
123478-HxCDD	0.45	0.22	0.30	2.43	0.29
123678-HxCDD	0.63	0.38	0.99	3.35	0.51
123789-HxCDD	0.88	0.61	1.01	4.72	0.69
1234678-HpCDD	6.67	4.87	15.03	43.57	5.75
OCDD	43.96	25.31	65.37	155.20	27.91
TOTAL PCDDs	52.97	31.48	83.18	211.38	35.41
2378-TCDF	4.71	2.72	3.85	20.89	2.09
12378-PeCDF	1.69	0.91	1.28	10.43	0.75
23478-PeCDF	2.97	1.34	2.12	15.00	1.43
123478-HxCDF	12.97	5.08	7.16	105.28	4.20
123678-HxCDF	4.88	1.94	2.69	34.75	1.65
234678-HxCDF	3.75	1.91	2.62	27.93	1.71
123789-HxCDF	0.56	0.32	0.47	3.98	0.28
1234678-HpCDF	43.80	15.82	22.69	367.35	14.29
1234789-HpCDF	5.02	2.00	2.14	48.86	1.49
OCDF	57.05	19.54	17.64	484.62	15.59
TOTAL PCDFs	137.40	51.58	62.66	1119.09	43.48
TOTAL PCDD/Fs	190.37	83.06	145.84	1330.47	78.89
I-TEQ PCDDs	0.537	0.265	0.751	2.896	0.394
I-TEQ PCDFs	4.802	2.110	3.069	31.951	1.919
TOTAL I-TEQs	5.339	2.375	3.820	34.847	2.313

** Limit of detection

Generally it was found that the total PCDF concentrations in sediments were higher than total PCDD concentrations with the exception of sediment C which exhibited total PCDD levels higher than total PCDF levels.

Regarding to PCDDs, it can be observed in Table 2 that OCDD exhibited always the highest values, followed by 1234678-HpCDD>123789-HpCDD>123678-HxCDD. The congener 2378-TCDD exhibited always the lowest levels.

Concerning PCDFs the general tendency observed was that OCDF exhibited the highest values followed by 1234678-HpCDF. The lowest values corresponded to 123789-HxCDF followed by

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12378-PeCDF < 23478-PeCDF. In general it can be said that in Venice Lagoon sediments, high chlorinated furan homologue groups prevail.

Relatively high I-TEQs are found in sediments from Porto Marghera harbour (34.85 ppt), especially when this value is compared with a preliminary quality objective of 20 ng/kg dw⁽²⁾.

Data found in this study were compared with a previous study carried out in the same lagoon⁽¹¹⁾. In that study data are provided for sediment samples taken in 1992 from Venice Lagoon in locations corresponding to the same sites C, D and E in this study. Total I-TEQs reported were 1.3; 7.8 and 0.7 for locations C, D and E respectively. Data presented in this study for the mentioned sites are slightly higher than those from Baldassarri et al.⁽¹¹⁾ but are in good agreement with the differences in pollution levels depending on the sampling location.

Table 3. Levels of PCDDs and PCDFs in crabs (pg/g wet weight).

Isomer	A	B	C	D	E
2378-TCDD	0.52	0.12	**0.23	0.74	**1.39
12378-PeCDD	0.65	0.40	0.54	1.40	**0.67
123478-HxCDD	0.41	0.45	0.60	1.14	**0.46
123678-HxCDD	0.28	0.14	0.23	0.65	**0.45
123789-HxCDD	0.35	0.21	**0.06	0.41	**0.55
1234678-HpCDD	0.40	0.39	0.66	1.10	**0.85
OCDD	1.03	1.01	2.56	2.52	1.35
TOTAL PCDDs	3.64	4.04	4.73	7.96	3.51
2378-TCDF	12.49	2.15	1.40	18.39	2.12
12378-PeCDF	2.88	0.50	0.39	7.01	**0.25
23478-PeCDF	2.09	0.51	0.40	5.45	0.45
123478-HxCDF	3.41	0.58	0.34	11.18	**0.63
123678-HxCDF	1.56	0.55	0.57	4.91	0.37
234678-HxCDF	1.06	0.38	0.43	2.53	**1.10
123789-HxCDF	1.07	0.82	1.29	1.98	1.99
1234678-HpCDF	1.35	0.48	0.44	4.65	**0.70
1234789-HpCDF	**0.14	0.12	**0.09	1.16	**0.95
OCDF	0.33	0.20	0.25	2.53	**1.85
TOTAL PCDFs	26.31	6.29	5.55	59.79	7.66
TOTAL PCDD/Fs	29.95	10.33	10.28	67.75	11.16
I-TEQ PCDDs	0.954	0.405	0.362	1.673	0.001
I-TEQ PCDFs	3.162	0.734	0.627	7.035	0.673
TOTAL I-TEQS	4.116	1.139	0.989	8.708	0.674

** Limit of Detection

Congener specific results of PCDDs and PCDFs in crabs from all the five locations studied, are presented in Table 3. It should be noted that all the seventeen 2,3,7,8 substituted PCDD/Fs were detected in samples from locations B and D. In location A there was just one congener not detected and individuals from location E exhibited the minimum number of detected congeners. Crabs collected at location D (Porto Marghera harbour) exhibited the highest pollution levels followed by A>E>C>B. Total PCDD/F levels ranged from 67.75 ppt in location D to 10.33 ppt in location B.

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The same general tendency observed for total PCDD and PCDF levels in sediments was also observed in crabs, being total PCDFs higher than total PCDDs. Regarding the isomer pattern, these are different compared to sediments and between locations. For PCDFs it can be observed that it was the 2,3,7,8-TCDF the congener which exhibited always the highest levels and 1,2,3,4,7,8,9-HpCDF and OCDF were the congeners exhibiting the lowest levels. In the case of PCDDs, OCDD frequently dominates in total concentration.

Total I-TEQs in crabs ranged from 8.71 ppt in location D to 0.67 in location E. These values do not exceed the established general reference values (10 to 20 TEQ ng/Kg) proposed by some Pollution Monitoring Programmes ⁽¹²⁾.

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