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Congener Specific Analysis of Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans in Crabs and Sediments from the Venice and Orbetello Lagoons, Italy

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This study is part of a more extensive research program to characterize pollution in two different lagoons in Italy using a multitrial biomarker approach in combination with residue analysis. It looks at levels of 2,3,7,8-chlorinated PCDDs and PCDFs in crabs and sediments from several locations in the Venice and Orbetello Lagoons, both affected by various types of pollution. The PCDD/F levels found in crabs and sediment from Venice and Orbetello Lagoons varied between sampling sites: the highest being from Porto Marghera harbor, a part of the Venice Lagoon characterized by high industrial impact. Principal Component Analysis was used to identify groups of similar sediment samples which can be correlated to possible sources of contamination. Four different sediment fingerprint patterns were recognized in the two-dimensional space formed by the two principal components which were mainly formed by a combination of highly chlorinated PCDDs and PCDFs.

Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) constitute a class of ubiquitous pollutants with a tricyclic aromatic structure, high chemical stability, and extremely poor water solubility. The presence of PCDDs and PCDFs in sediments of waterways in industrialized and heavily populated areas is an environmental problem that has received considerable attention in recent years (*1*). There is growing evidence that these compounds are extremely harmful to marine and freshwater ecosystems, especially when they bioaccumulate through aquatic foodwebs (*2*). PCDDs and PCDFs are formed as a byproduct of various chemical and combustion processes (*3*) and enter the aquatic environment from the atmosphere (*4*) and as direct discharges from industrial sources, sewage treatment plants, and storm drains (*5*).

While the PCDD/F congener patterns in sediments contaminated exclusively by atmospheric deposition are dominated by OCDD, sediments contaminated directly by industrial discharges contain complex patterns of PCDD/F congeners. Multivariate statistical techniques such as Principal Components Analysis (PCA) have been successfully used to interpret data and to make comparisons between PCDD/F patterns in sediments and potential sources (*5*−*7*), although the difficulties which could be found due to environmental factors which could alter the original pattern (*8*−*10*). The PCA was applied to compare patterns of the studied sediments with different emission sources of PCDD/Fs in order to determine which types of pollution sources are responsible for the presence of these compounds in the samples studied.

This study is part of a more extensive research program seeking pollution in two different lagoons in Italy using a multitrial biomarker approach. It looks at levels of PCDDs and PCDFs in crabs and sediment taken from different locations in the Venice and Orbetello Lagoons. The Venice Lagoon is 52 Km long and connects with the northern Adriatic Sea. Many streams and outlets conveying industrial effluent, urban sewage, and agricultural runoff discharge into the lagoon which has limited water exchange with the open sea through three channels. Heavy motorboat traffic on the lagoon contributes directly and indirectly to the contaminant load. The Orbetello Lagoon is an old part of the Mediterranean located between the Tuscan coast and Monte Argentario. It has a surface area of 2700 ha and is trapezoid shaped. The Lagoon is divided in two main basins: Ponente and Levante. Water exchange with the Mediterranean Sea occurs through two channels in the Ponente lagoon and one channel in the Levante lagoon. There were two main reasons for the choice of crabs and sediments for this study. Studying sediments is useful for understanding pollution in a given area and provides important parameters with which to evaluate the effects on ecosystems (*11*). The crab *Carcinus aestuarii* was used as a bioindicator organism in combination with a multitrial biomarker approach for ecological risk assessment (*12*). There are several advantages in using invertebrates in ecotoxicology: they are major components of all ecosystems, and populations are often numerous, so that samples can be taken without significantly affecting population dynamics (*13*). Moreover invertebrates constitute 95% of all animal species (*14*) and have the advantage over fish in that they remain in a confined area. In addition crabs are also unique in that they do not readily metabolize non 2,3,7,8-substituted PCDD/F congeners.

Materials and Methods

Sampling Sites. *Sediment*. In September 1995, samples of surface sediment (upper 5 cm) were obtained using a stainless steel box from five different sites in the Venice Lagoon (see Figure 1). Each of the sites was characterized by different types of pollution:

Station **1**, Giudeca Island: area with a high urban impact from the city of Venice with a heavy pollution due to a high motorboat traffic and the presence of untreated sewage.

Station **2**, Pellestrina: area selected as control site, relatively remote from industrial sources and with moderate water exchange.

Station **3**, Chioggia harbor: zone of the lagoon affected by a high harbor activity and with ample water exchange.

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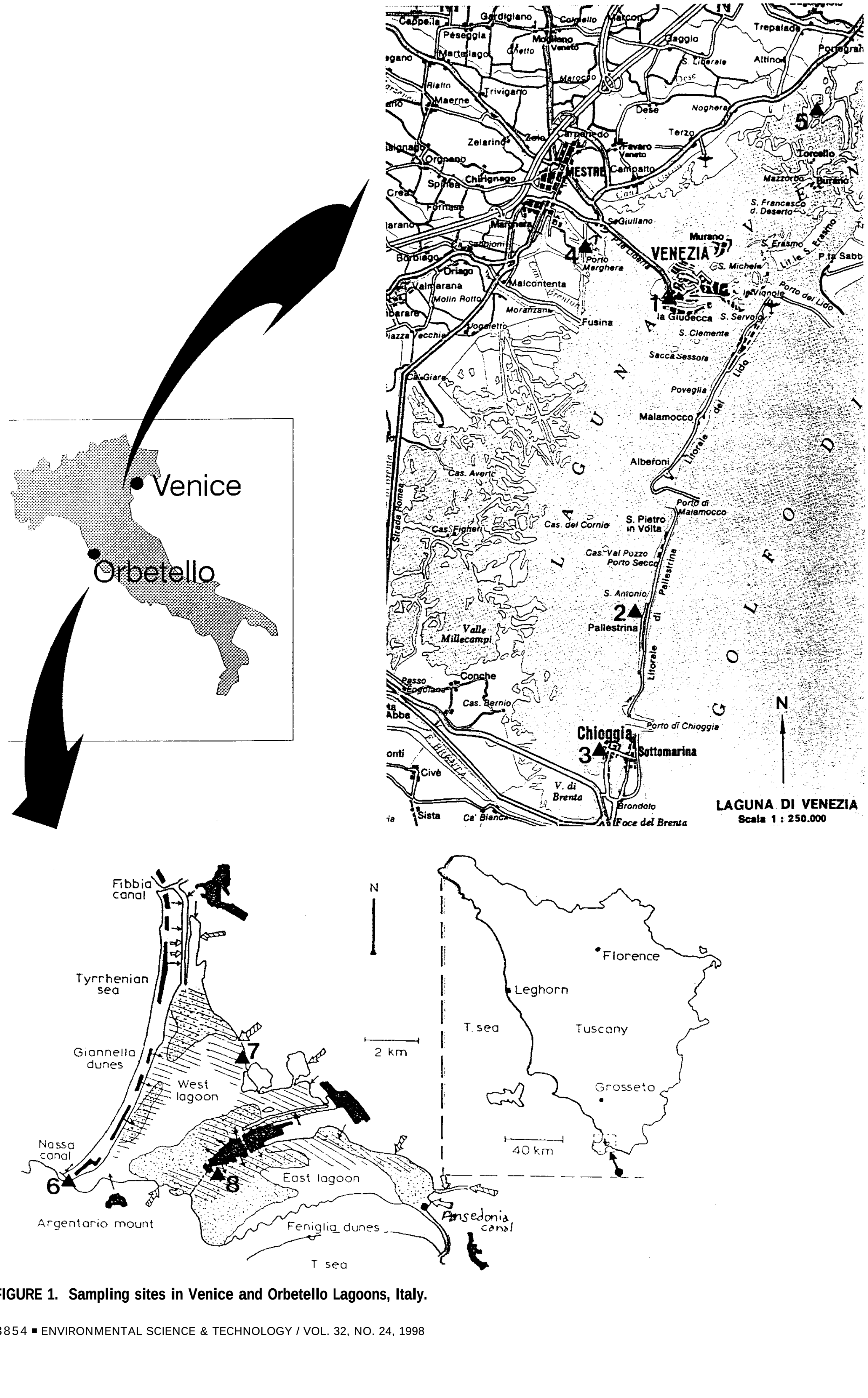

FIGURE 1. Sampling sites in Venice and Orbetello Lagoons, Italy.

Station **4**, Porto Marghera: area with a high industrial impact due to chemical and oil refining plants and with slow water exchange.

Station **5**, Dese River: zone with a slow water exchange and affected by an agricultural impact.

In June 1995, samples of surface sediment were obtained using a stainless steel box from three selected sites in Orbetello Lagoon (see Figure 1).

Station **6**, Santa Liberata: located far from any industrial source and with ample water exchange, since it is situated near the exchange channel with the sea. Control site.

Station **7**, Sitoco: Near an industrial effluent polluted by PVC containing materials, an area of the lagoon with slow water exchange.

Station **8**, Orbetello: Sewage treatment plant from Orbetello city with moderate water exchange.

Freshwater sediment was not sieved as particle size was nearly always less than 63μ.

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 −80 °C until analysis.

In the Orbetello Lagoon 36 male specimens of *Carcinus aestuarii* were obtained from station A, which was selected as the control site since here the antropic impact is minimum. 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. After this period, the crabs were killed, and their tissues stored at −80 °C until analysis.

Analytical Determination. Extraction and Clean Up. Crabs. Extraction and clean up were performed as described in detail previously (*15*). Basically this consisted of low-pressure chromatography on neutral and base-modified silica gel and activated carbon dispersed on glass fibers. Three fractions were eluted from the carbon column for each sample. These contained ortho-substituted PCBs, nonortho-substituted PCBs, and PCDD/Fs, respectively. Further clean up was done using silica gel impregnated with sulfuric acid and Florisil.

Prior to the initial extraction of samples, a mixture of $^{13}C_{12}$ PCDD/Fs and nonortho-substituted PCBs internal standards was added. Samples of between 3 and 5 g of edible crab tissue (including thoracic, claw, leg, and tail meat) were used for analysis. For each sampling site from the Venice Lagoon the biological material of five to eight crabs was pooled. In the case of the Orbetello Lagoon the biological material of 12 crabs was pooled for each station.

Sediment. PCDD/Fs analysis was performed on approximately 20 g of sediment dried, spiked with a mixture of 15 [$^{13}C_{12}$], and Soxhlet extracted with toluene for at least 24 h. Clean up was performed as previously described (*16*). Basically this consisted of a multilayer column containing neutral, acid, and basic modified silica gel. Further cleanup was carried out on a second column containing Florisil. The organic carbon content in the sediment was determined using the method of Gaudette et al. (*17*).

Quantification. Resolution and quantification of PCDDs, PCDFs, and coplanar PCBs were performed by HRGC−HRMS using a VG AutoSpec Ultima (VG Analytical, Manchester, UK) coupled to a Fisons Series 8000 (8060) gas chromatograph. A fused silica capillary column DB-5 and a DB-DIOXIN (60 m, 0.25 mm id., 0.25 μm film thickness, J&W Scientific, USA) were used. Helium at a column head pressure of 175 Kpa was used as the carrier gas. A minimum resolution of 10 000 was used when operating with the HRMS instrument. Methods blanks were routinely analyzed, and no contributions were detected. Total values reported were calculated assuming that all values less than the limit of detection (LOD) are equal to the half the LOD.

Multivariate Analysis. *Database.* A database containing 83 pieces consisting of sediments polluted by different emission sources of PCDD/Fs and some typical effluents was gathered from the available literature (*5*, *6*, *18*−*33*). Table 1 shows all the different emission sources selected and sediments included in the database and the identification symbol used in figures. For the multivariate analysis, a single matrix was created, containing analytical data of the 2,3,7,8 substituted PCDD and PCDF congeners from the database and analytical data corresponding to the sediments considered in this study (5 from Venice and 3 from Orbetello). Chemometric comparison was done using Principal Component Analysis (PCA), which is a Multivariate Analysis technique for dimension reduction (*34*, *35*).

Data were scaled in order to minimize any statistical bias associated with order of magnitude differences in chemical concentrations. Data were normalized by expressing the concentration of individual variables as a percentage of the combined sum of total variables. The statistical analysis were carried out on a Pentium PC "Statgraphics" statistical software (V 5.0, STSC, Inc., U.S.A.).

Results and Discussion

Levels of 2,3,7,8-substituted PCDD and PCDF congeners and calculated I-TEQs (*36*) in all samples studied are shown in Table 2. Since crabs and sediments are known to contain non 2,3,7,8-congeners which coelute with some of the tetra- to hexa 2,3,7,8-substituted congeners, a polar column was used for those critical congeners in order to avoid over estimations of the calculated I-TEQs. Values corrected taking this fact into account are presented in Table 2 for all those samples were differences in the total estimated I-TEQ were higher than a 5%. In general congeners over estimated in sediments were 1,2,3,7,8,9-HxCDD, 2,3,7,8-TCDF, 2,3,4,7,8-PnCDF, and 1,2,3,4,7,8-HxCDF. In the case of crabs, over estimated congeners were 2,3,7,8-TCDD and 2,3,7,8-TCDF.

Sediments from the Venice Lagoon. All 2,3,7,8-substituted PCDD/Fs were detected in almost all sediments studied with differences between sampling sites. Total PCDD/F levels ranged from 78.89 ppt in site 5 to 1330.47 ppt in site 4. Sample 4 (Porto Marghera harbor) had the highest levels followed by 1 > 3 > 2 > 5.

Total PCDF levels were generally higher than total PCDD concentrations with the exception of sediment from site 3 (Chioggia harbor) which had total PCDD levels higher than total PCDF levels.

Regarding PCDDs, OCDD had the highest values in all cases, followed by 1,2,3,4,6,7,8-HpCDD > 1,2,3,7,8,9-HpCDD > 1,2,3,6,7,8-HxCDD. The congener 2,3,7,8-TCDD always had the lowest levels in all sediments studied. In the case of PCDFs, OCDF generally had the highest values followed by 1,2,3,4,6,7,8-HpCDF. The lowest values where those of 1,2,3,7,8,9-HxCDF followed by 1,2,3,7,8-PeCDF and 2,3,4,7,8-PeCDF. In general, therefore, highly chlorinated homologue groups are prevalent in Venice Lagoon sediments.

Figure 2 shows all the normalized congener patterns in sediments from the Venice Lagoon. Two main patterns can be distinguished, one characterized by high OCDF and PCDF levels higher than PCDD levels corresponding to stations 1 and 4. This indicates that samples appear to be most affected by an industrial source rich in OCDF. This could be related to the production of ethylene dichloride (EDC) as proposed in a previous work (*37*). A second type of pattern is characterized by high OCDD corresponding to stations 3 and 5 which could be related to combustion resulting from local marine traffic. Sediment from station 2 could be

TABLE 1. Emission Sources and Polluted Sediments by PCDD/Fs Included in the Database, Used To Be Identified in Figure 4 (Parts A and B)

code	emission source: location	emission source: sediments affected by	ref
A	Lake Valjarki (Finland)	fungicide (KY-5)	18
B	Er-Jen River (Taiwan)	open air incinerator activities, discharge of PCBs and PCPs	19
C	Wan-Li (Taiwan)	waste incinerator sites for metal reclamation	20
D	Taiwan	chlorophenol manufacturing plant	21
E	Chemieharbor (Netherlands)	vinyl chloride monomer production	6
F	Friefjorden (Norway)	magnesium processing plant	22
G	Black Rock Harbor (U.S.A.)	transformer fluids containing PCBs and urban pollution	7
H	New Bedford Harbor (U.S.A.)	incinerator fly ash and fluids containing PCBs	7
I	Providence River (U.S.A.)	chlorophenols manufacturing plant and urban pollution	7
J	Eagle Harbor (WA, U.S.A.)	PCBs and PCPs	7
M	Hamburg Harbor (Germany)	production and use of chlorinated products, mainly PCPs	23
N	St. Laurensharbor (Netherlands)	airborne fly ash from chemical waste incinerator	6
O	Inner Stockholm archipelag (Sweden)	urban pollution (automobile and shipping traffic, oil heating systems, one municipal waste incinerator (MSW)	24
P	Stockholm arch (Sweden)	MSW, car exhausts, cooper smelter, and steal mills	25
R	Lake Ladoga (Finland)	paper mills, thermolisis of PCPs, metal recycling combustion	26
S	Newark Bay (NY, U.S.A.)	urban pollution, automobile and shipping traffic, MWI, ChW	5
T	Neward Bay (NY, U.S.A.)	chemical chlorinated industrial activities (PCPs, PCBs)	5

code	emission source: sample	emission source: effluents	ref
K	waste treatment sludge	pulp and paper industry	27
L	sludge from graphite electrodes	production and use of chloroalkali	28
Q	tetrachlorobenzoquinones	chlorinated products	29
	dioxazine dyes and pigments		30
	chloranil and carbazol violet		31
V	PCV-containing materials fire	combustion of PVCs	32
X	commercial PCPs	pentachlorophenol	33
Y	commercial Na-PeCl-phenate	Na-pentachlorophenate	33

considered a mixture of both patterns described previously with a high contribution of OCDD and OCDF in similar quantities.

Total calculated I-TEQs ranged from 2.17 ppt in location 5 to 26.67 ppt in location 4. PCDDs constituted between 8 and 20% of the total I-TEQ, while PCDFs contributed at least 80%. Relatively high I-TEQs were found in sediments from the Porto Marghera harbor (26.67 ppt), especially when this value is compared with a preliminary quality objective of 20 ng/kg dw (*1*).

The present results were compared with those of a previous study carried out in 1992 in which sediment was sampled at the same sites 3, 4, and 5 (*38*). Total I-TEQs were 1.3, 7.8, and 0.7 ppt, respectively. Our figures are slightly higher but reflect the same tendencies. Instead our figures differ considerably from values reported by Fattore et al. (*37*) who found the highest I-TEQs in Venice which would correspond to location 1 in the present study.

Crabs from the Venice Lagoon. All 17 2,3,7,8-substituted PCDD/Fs were detected in crabs from Pellestrina (2) and Porto Marghera (4). Sixteen congeners were detected in crabs from site 1, 14 in site 3, and only 5 in crabs from site 5. Total PCDD/F levels ranged from 9.01 ppt in site 2 to 67.75 ppt in site 4. Crabs from location 4 had the highest PCDD/F levels followed by those from sites 1 > 5 > 2 > 3.

The general trend in total 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 as can be seen in Figure 2. Among PCDFs, 2,3,7,8-TCDF always had the highest levels and 1,2,3,4,7,8,9-HpCDF and OCDF the lowest unlike in sediments. Among PCDDs, OCDD frequently dominated in total PCDD concentrations. The congener pattern found in these crabs was quite similar to that found in other studies (*39*), dominated by 2,3,7,8-TCDF, a congener typical of the emissions of chloralkali plants (*40*−*42*). Total I-TEQs ranged from 4.24 ppt in site 4 to 1.10 ppt in crabs from site 3. These values do not exceed the established reference values (10−20 TEQ ng/Kg) proposed by some Pollution Monitoring Programs (*43*).

Sediments from the Orbetello Lagoon. Almost all 2,3,7,8-substituted PCDD/Fs were detected in all sediments studied. The highest levels were found in location 8, while location 6 exhibited the lowest levels. Total PCDDs were always higher than total PCDFs in contrast with the tendency found in sediments from Venice. In the case of PCDDs, OCDD and 1,2,3,4,6,7,8-HpCDD always had the highest values, and the lowest levels were exhibited by 2,3,7,8-TCDD and hexachlorinated congeners. In the case of PCDFs, OCDF generally had the highest values as well as 1,2,3,4,6,7,8-HpCDF which in some cases was slightly higher than OCDF. The lowest values were those of pentachlorinated congeners. In general, therefore, highly chlorinated homologue groups are prevalent in Orbetello Lagoon sediments, OCDD and OCDF being the predominant congeners as can be seen in Figure 3. Total calculated I-TEQs ranged from 0.39 ppt in location 6 to 7.27 ppt in location 7. None of this values exceeded a quality objective of 20 ng/kg dw (*1*).

Crabs from the Orbetello Lagoon. Fifteen congeners were detected in crabs from site 6, 9 in crabs from site 8, and only 6 in crabs from site 7. The general trend in total PCDD and PCDF levels in sediments was different in crabs, total PCDFs and total PCDDs being almost equal in the three stations studied, each of them contributing almost 50% to the total PCDD/Fs value. The isomer patterns (Figure 3) were similar to those of sediments, OCDD, OCDF, 1,2,3,4,6,7,8-HpCDD, and 1,2,3,4,6,7,8-HpCDF always being the congeners exhibiting the highest levels. Total I-TEQs ranged from 1.12 ppt in site 6 to 4.28 ppt in crabs from site 8. These values did not exceed the established reference values (10−20 TEQ ng/Kg) (*43*).

TABLE 2. PCDD and PCDF Levels in Sediments (S) and Crabs (C) from Venice (Stations 1−5) and Orbetello (6−8) Lagoons (pg/g Dry Weight in Sediments or Wet Weight in Crabs) and Calculated I-TEQs[a]

isomer	S1	C1	S2	C2	S3	C3	S4	C4	S5	C5	S6	C6	S7	C7	S8	C8
2378-TCDD	0.08	0.52	0.07	0.12	0.13	0.23[b]	0.40	0.94	0.06	1.39[b]	0.02	0.47[b]	0.40[b]	1.87[b]	0.34[b]	0.56[b]
12378-PeCDD	0.30	0.65	0.05[b]	0.40	0.35	0.54	1.71	0.92	0.20	0.67[b]	0.10	0.42	0.44[b]	1.87[b]	0.60	0.50[b]
123478-HxCDD	0.45	0.41	0.22	0.45	0.30	0.60	2.43	0.74	0.29	0.46[b]	0.09	0.29	0.66	1.87[b]	1.27	0.25[b]
123678-HxCDD	0.63	0.28	0.38	0.14	0.99	0.23	3.35	0.62	0.51	0.45[b]	0.08	0.15	2.32	1.87[b]	2.41	0.33[b]
123789-HxCDD	0.88	0.35	0.61	0.21	1.01	0.06[b]	4.72	0.36	0.69	0.55[b]	0.10	0.32	2.41	1.87[b]	2.45	5.74
1234678-HpCDD	6.67	0.40	4.87	0.39	15.03	0.66	43.57	0.82	5.75	0.85[b]	0.74	1.71	25.47	0.70[b]	47.72	11.78
OCDD	43.96	1.03	25.31	1.01	65.37	2.56	155.20	1.78	27.91	1.35	3.77	9.55	193.61	49.43	335.27	44.95
2378-TCDF	4.71	12.49	2.72	2.15	3.85	1.40	20.89	11.47	2.09	2.12	0.52	0.88	11.21	0.80[b]	5.24	6.27
12378-PeCDF	1.69	2.88	0.91	0.50	1.28	0.39	10.43	2.60	0.75	0.25[b]	0.13	0.24	4.11	0.65[b]	1.51	0.16[b]
23478-PeCDF	2.97	2.09	1.34	0.51	2.12	0.40	15.00	2.81	1.43	0.45	0.23	0.33	5.74	0.63[b]	1.89	0.17[b]
123478-HxCDF	12.97	3.41	5.08	0.58	7.16	0.34	105.28	4.32	4.20	0.63[b]	0.42	0.73	10.01	1.06[b]	5.18	8.18
123678-HxCDF	4.88	1.56	1.94	0.55	2.69	0.57	34.75	2.31	1.65	0.37	0.23	0.57	2.93	0.87[b]	1.94	5.09
234678-HxCDF	3.75	1.06	1.91	0.38	2.62	0.43	27.93	1.69	1.71	1.10[b]	0.24	0.87	3.72	13.67	2.64	10.40
123789-HxCDF	0.56	1.07	0.32	0.82	0.47	1.29	3.98	1.22	0.28	1.99	0.16	0.86	0.85	4.50	1.74[b]	0.36[b]
1234678-HpCDF	43.80	0.35	15.82	0.48	22.69	0.44	367.35	2.70	14.29	0.70[b]	0.71	2.75	11.97	41.90	16.66	30.10
1234789-HpCDF	5.02	0.14[b]	2.00	0.12	2.14	0.09[b]	48.86	0.41	1.49	0.95[b]	0.14	0.23[b]	1.28	8.97	1.39[b]	0.76[b]
OCDF	57.05	0.33	19.54	0.20	17.64	0.25	484.62	0.65	15.59	1.85[b]	0.81	3.98	15.05	27.12	7.78[b]	24.69
TOTAL PCDFs	137.40	26.31	51.58	6.29	62.66	5.55	1119.09	30.18	43.48	7.65	3.59	11.32	66.87	98.15	40.51	85.45
TOTAL PCDDs	52.97	3.64	31.48	2.72	83.18	4.73	211.38	6.18	35.41	3.51	4.90	12.67	224.89	54.43	389.89	63.28
TOTAL PCDD/Fs	**190.37**	**29.95**	**83.06**	**9.01**	**145.84**	**10.28**	**1330.47**	**36.36**	**78.89**	**11.16**	**8.49**	**23.99**	**291.76**	**152.58**	**430.40**	**148.73**
TOTAL I-TEQs	**4.90**	**4.10**	**2.22**	**1.13**	**3.60**	**1.10**	**31.10**	**5.25**	**2.17**	**1.70**	**0.39**	**1.12**	**7.27**	**3.93**	**4.52**	**4.28**
	3.85[a]	**3.670**[a]					**26.67**[a]	**4.24**[a]								

[a] Calculated I-TEQ values assuming no co-elutions. [b] Limit of detection.

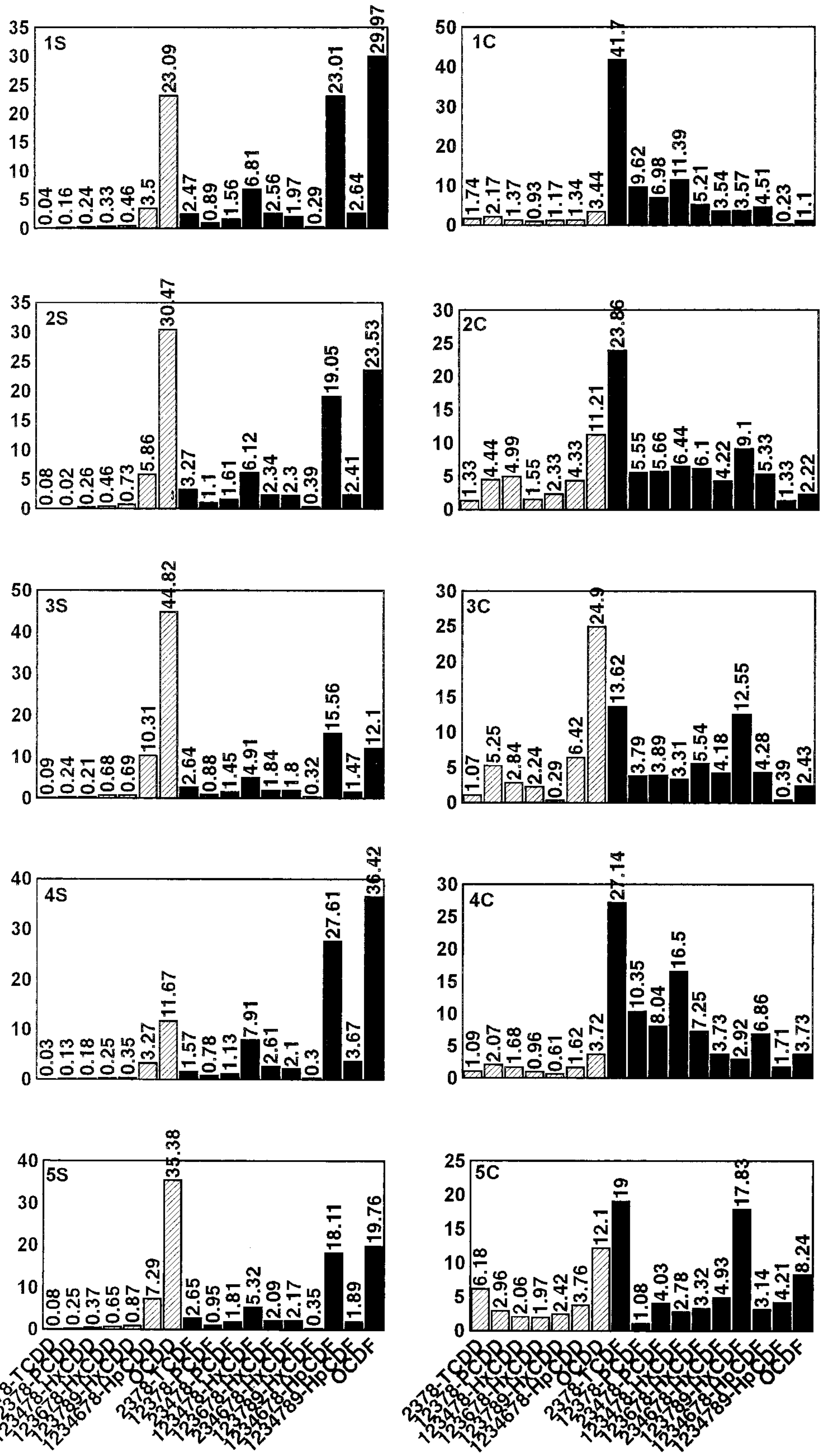

FIGURE 2. 2,3,7,8 congener pattern normalized to the sum of total PCDD/F in sediments (A) and crabs (B) from Venice Lagoon.

When patterns in crabs from both lagoons are compared, some interesting observations can be made. In Orbetello lagoon, crabs taken in Station 6 show a pattern similar to sediment from the same station. This could be a situation in which equilibrium has been reached with the pollution input. In contrast, the situation changes considerably in stations 7 and 8. Crabs which were living in stations 7 and 8 for a 15-days period show a pattern which differs considerably from those found in sediments where they were kept. Based on previous studies (*44*), this means that patterns from crabs in this case show the emission pattern from the wastewater almost unchanged. It is also quite interesting to

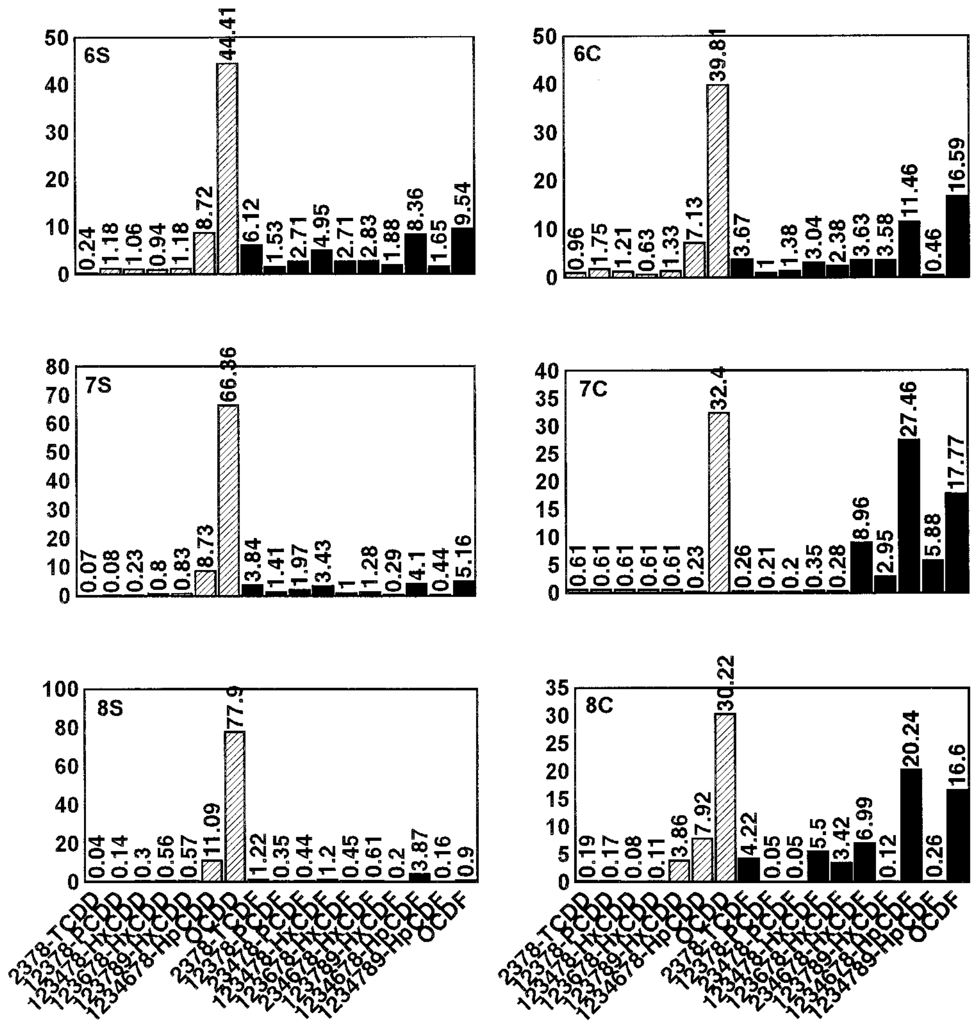

FIGURE 3. 2,3,7,8 congener pattern normalized to the sum of total PCDD/F in sediments (A) and crabs (B) from Orbetello Lagoon.

note the differences between the Orbetello and Venice Lagoons; in station 6 from Orbetello an equilibrium can be seen between crabs and sediments, in contrast with crabs from stations studied in Venice where all crabs exhibited patterns different from the sediments from where they were taken.

Multivariate Analysis. The principal components calculation from the normalized data set (91 objects and 17 variables) indicated that the first two principal components accounted for 77.3% of the total variability. The first principal component, PC1 (retained 59.6 of the original variance of the data set), was a combination of the highest chlorinated PCDD/Fs congeners, the HpCDF1, OCDF, and OCDD. The second first principal component, PC2 (retained 17.7% of the total variability), was mainly formed by a combination of HpCDD, OCDD, and OCDF.

Figure 4 (parts A and B) shows the two-dimensional principal components score and loading plots for the pattern of the 17 PCDD/F congeners in sediments from the Venice and Orbetello Lagoons and sediments affected by different emission sources. Various fingerprint patterns could be recognized in the two-dimensional space formed by the first two components (Figure 4B).

Group I. Sediments polluted by chemical activities involved in the production and use of various chlorinated products, such as pentachlorophenol (I, J), transformed fluids that contain PCBs (G), and both together (J, T); effluents related with chemical activities, such as paper mills (K), production, and use of pentachlorophenols, and other chemical products such as dyes, dioxazines, and pigments (X, Q). These are characterized by a high OCDD content and low OCDF values.

Group II. Sediments polluted by magnesium production plants (F), and effluents from the combustion of different types of PVC (V), chloroalkali industrial use (L), characterized by high content of 2,3,7,8-substituted penta- and hexafurans.

Group III. Sediments mainly polluted by chemical activities such as vinyl chloride monomer production (E), discharge of PCPs (D). These are characterized by high OCDF content, medium values of OCDD, and low HpCDD content.

Group IV. Sediments mainly polluted by combustion emissions, such as incineration of chemical products (N), sediments affected by various combustion sources, including marine traffic (O, P), incinerator fly ash from PCB transformers (H), various combustion sources (P), jointly with some chemical activities (J, M). They are characterized by high HpCDD, OCDD, and OCDF contents and lower content of the lower chlorinated PCDD/Fs.

Sediments from Venice and Orbetello are mainly differentiated by the first principal component (PC1). The second principal component (PC2) does not constitute a significant differentiating factor between all the sediments studied.

Sediments from the Venice Lagoon. The five sediments from Venice Lagoon are distributed from the origin to the negative end of the PC1 axis. Pattern from sediments 1 and 4 are very closed in the two-dimensional space, and they are similar to sediments affected by the chemical industry, such

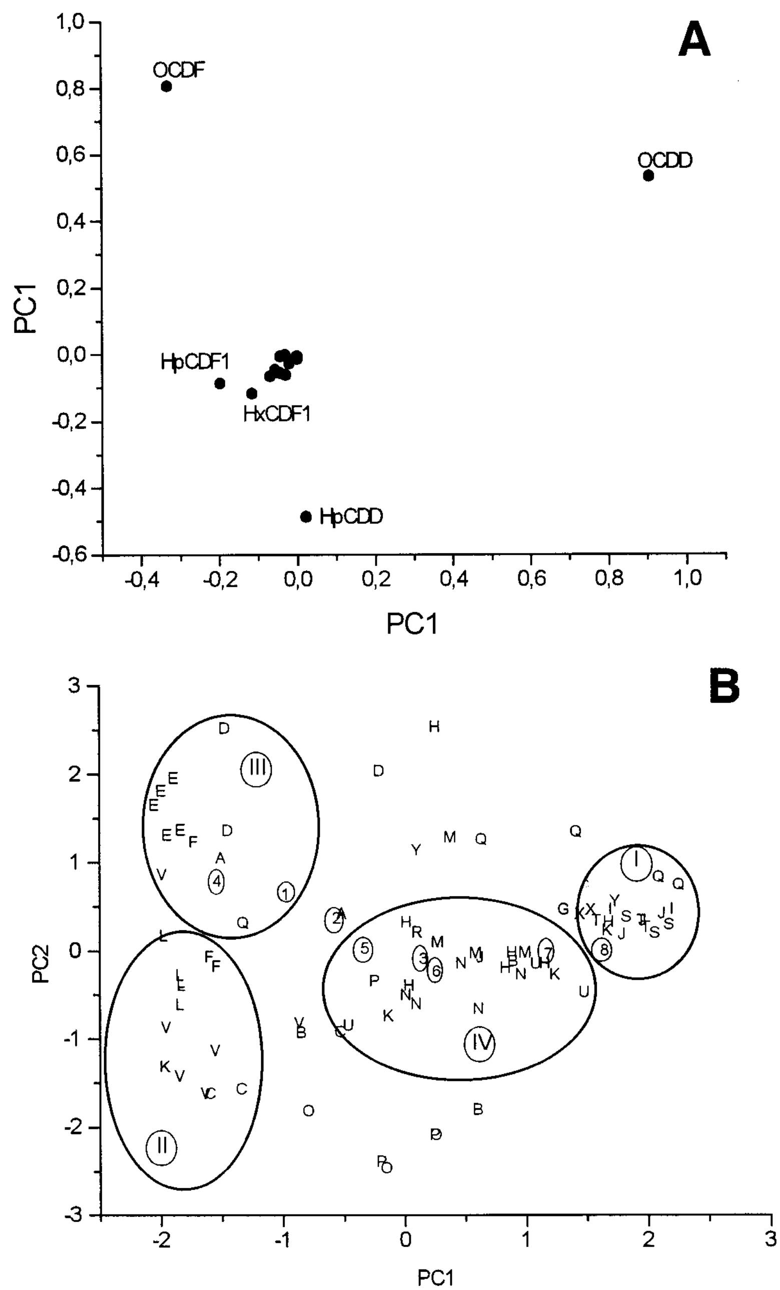

FIGURE 4. Two-dimensional principal components loading (A) and score (B) plots of the normalized 2,3,7,8-substituted congeners in sediments from Venice and Orbetello Lagoons and sediments affected by different emission sources.

as sediments polluted by a magnesium plant (F), sediments affected by vinyl chloride monomer production (E), and sediments near a PCPs production plant (D). Patterns from sediments 3 and 5 are similar mainly to sediments affected by combustion activities. Thus, they are close to sediments affected by incinerator fly ash and fluids containing PCBs (H), airborne fly ash from chemical waste incinerators (N), and those affected by production of various chlorinated products, including PCPs (M). Sediments from location 2 are near to points corresponding to locations 1 and 5 in the two-dimensional plot (Figure 4B) and very close to sediments affected by some fungicide application (A), but they cannot be included in any of the four classes previously described.

Sediments from the Orbetello Lagoon. All the sediments from Orbetello Lagoon are located closely in the two-dimensional plot defined by the two first principal components, but some differences could be observed. For example, sediments from location 6 could be included in the same cluster where are included sediments from location 3 from the Venice Lagoon and are associated with chemical activities and chemical products combustion (J, M, N), and they also are near to the pattern corresponding to sediments contaminated by PCBs (H). Sediments from location 7 are related to chemical and combustion activities. Thus, the pattern for these sediments is close to that of sediments affected by manufacturing and use of PCBs (H), open air incineration (B), and emissions from waste paper mills (K). Sediments from station 8 are related to chemical chlorinated industrial activities, mainly related to PCBs and PCPs (G, X, Q, S, I) and waste paper mills (K).

Several environmental factors can modify the distributions and levels of PCDDs and PCDFs in sediments. Due to the fact that sediments act as a reservoir, hydrological conditions may increase the opportunity for redistribution of sediments-bound PCDDs and PCDFs (*45*, *46*). These compounds have been shown to be susceptible to slow biodegradation (*47*), photolysis (*8*), and volatilization (*8*, *47*). These processes as well as others will act to modify the congener patterns in bottom sediment (*48*). Therefore, some caution is necessary when relating PCDD and PCDF residue levels to particular sources (*49*). Despite these uncertainties, pattern recognition is a useful way of identifying groups of similar environmental samples, which can then be correlated to possible sources (*7, 50*). Chemometric methods can assist in the identification of sources of contamination.

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