PCDD and PCDF contamination patterns in clam and sediment samples collected from congruent sampling sites in the Venice lagoon. I. Sediments

Miniero R., Brambilla G., Dellatte E., Ferri F., Fochi I., Fulgenzi A.R., Iacovella N., Iamiceli A.L., Ingelido A.M., and di Domenico A.

Department of the Environment and Primary Prevention, Istituto Superiore di Sanità, 00161 Roma, Italy

Introduction

The Venice lagoon was subjected to several investigations to determine the contamination levels of the superficial bottom sediments. Among the many chemicals determined, polychlorinated dibenzodioxins (PCDDs) and dibenzofurans (PCDFs) were considered with particular attention for their relevant toxic properties. In addition, based on previous evidence PCDDs and PCDFs were confirmed to be the best descriptors of local anthropogenic impact(s) in the lagoon.[1] Therefore, it appears to be of great interest to assess the profile differences among sediment and clam samples collected in the same sites. In this paper the PCDD and PCDF profiles detected in sediment samples are subjected to principal component analysis (PCA).

Materials and methods

Sampling locations were selected on the basis of a Venice lagoon subdivision in virtual risk areas (RA's).[1] These areas (identified with RA's 1 through 6, the latter for open sea) were classified according to theoretically decreasing exposure levels (Table 1). Lagoon sediment sampling and pre-treatment processing to produce the matrices for analysis were reported elsewhere.[2] For the assessment of chlorinated analytes, analytical samples were spiked with fully ^{13}C-labelled (internal) standards. The analytical procedure was adapted from the US EPA Method No 1613.[3] Analytes were quantified by HRGC-LRMS(SIM) or -HRMS(SIM). Good laboratory practice and QA/QC protocols were applied throughout. PCA was applied to PCDD and PCDF analytical data. For each sample, congener concentrations were normalized against the pertinent cumulative analytical concentration Σ_{17}(PCDDs+PCDFs, pg/g), the latter obtained by adopting the medium bound approach when dealing with limits of determination. Samples (cases) and congeners (variables) with an high incidence (>40 %) of non-detects throughout the samples were removed to minimize the non-detect impact on PCA.[4]

Results and discussion

Table 1 summarizes congener-specific contributions (%), total concentration levels (pg/g), and virtual risk areas of the sediment samples considered in the study. Table 2 and 3, respectively, show the eigenvalues (>1) of selected components and their variances (%), and the sample scores. Four components (Table 2) were extracted from the data reported in Table 1, accounting for a cumulative percentage of 86 %. The first component (PC 1), characterized by a relevant variance of 40 %, describes a general subdivision of samples collected from high-to-medium exposed sites and background areas. PC 2 (variance, 28 %) describes the structure of the contamination pattern in samples not directly exposed to industrial sources nor to background influence but rather under an "urban environment" impact (Table 2; Figures 1a and 1b). PC's 3 and 4 (cumulative variance, 18 %) suggest further interpretation of the clusters identified by PC's 1 and 2. In the score plot of Figure 1a, the samples on the left side are clumped together (Table 3; Figure 1a): from the factor loadings plot it can be observed that f8, f9, and f10 are among the dominating variables determining the distribution (Figure 1b). The aforesaid samples, characterized by high negative scores (<–1.17) in Table 3, were collected inside the industrial channels and from sites close to the Malamocco-Marghera channel. The high positive scores (>+2.95) (Table 3) in PC 1 belong to samples collected from background areas, where the prevalent congeners are d6 and d7 and, to a small extent, d4, d5, f1, f2, and f3 (Table 3 and Figure 1b). In PC 2, the samples showing the highest positive scores (>+1,82) (Table 3) are F1, F2, F3, F4, F5, and 10. These samples were collected in the central part of the lagoon, from sites close to the Venice urban settlement. The most important variables characterizing these samples are d2, d3, f2, f5, and f7. In PC 2 the highest negative scores are for samples collected from industrial and background areas, respectively. On the whole, the PCDD and PCDF congener patterns detected in the lagoon area have industrial, urban, or background features. Furthermore, patterns may exhibit clear differences of congener

profiles, thus reflecting local exposure conditions. In conclusion, the original subdivision in five virtual risk areas can be reduced to three by taking into account the scores for samples presenting the highest values under PC's 3 and 4. According to this evaluation, RA's 2 and 3 appear to overlap each other, whereas RA's 4 and 5, although not completely overlapping, appear to present similar impacts.

Table 1. Selected relative congener concentrations (%) and total analytical concentrations (pg/g) of PCDDs (d1 through d7) and PCDFs (f1 through f10) in sediment samples, and sample classification in virtual risk areas.

Sample/Site	*d2*	*d3*	*d4*	*d5*	*d6*	*d7*	*f1*	*f2*	*f3*	*f4*	*f5*	*f7*	*f8*	*f9*	*f10*	*Total*	*RA*
X1	0.05	0.11	0.10	0.09	1.47	8.40	0.37	0.73	0.29	3.70	1.44	0.76	13.4	3.21	65.7	2478	1
E1	0.10	0.17	0.24	0.10	3.01	13.5	0.91	1.11	0.50	4.48	1.70	1.21	17.3	3.02	52.5	926	1
E2	0.10	0.16	0.19	0.14	2.39	12.4	0.95	1.00	0.51	4.34	1.61	1.15	17.0	3.22	54.5	813	1
E3	0.12	0.16	0.22	0.17	2.90	14.6	0.98	1.13	0.60	4.11	1.79	1.27	17.7	3.25	50.8	84.0	1
E4	0.15	0.20	0.28	0.18	3.40	15.7	1.40	1.07	1.00	4.70	1.97	1.48	17.8	3.17	47.1	75.7	2
E5	0.10	0	0.19	0	2.25	12.9	0.78	0.56	0.52	3.16	1.23	0.70	22.4	3.45	51.4	117	1
E6	0.16	0.24	0.35	0.17	3.29	17.5	1.53	1.19	0.90	4.56	2.12	1.70	16.8	3.09	46.1	145	2
F1	0.20	0.28	0.46	0.29	4.02	18.7	1.75	1.49	0.92	4.70	2.07	2.05	17.1	3.12	42.5	59.0	2
F2	0.17	0.23	0.36	0.27	3.56	18.4	1.45	1.47	0.80	5.75	2.52	1.62	19.7	2.93	40.4	152	2
F3	0.39	0.46	0.55	0.52	4.69	22.9	2.72	1.55	1.15	4.84	2.06	2.48	14.8	2.38	38.2	28.7	3
F4	0.17	0.23	0.32	0.29	3.88	20.0	1.50	1.56	0.74	5.59	2.22	1.61	19.7	2.81	39.1	318	2
F5	0.33	0.37	0.52	0.53	4.26	23.3	2.53	1.73	1.22	4.99	2.20	2.36	17.4	2.38	35.4	30.4	3
Chioggia 1	0	0	0	0	6.86	47.7	3.34	1.15	1.15	2.15	1.24	1.61	8.4	1.73	21.3	8.68	5
4	0	0.20	0.36	0.28	2.83	14.2	2.93	1.24	0.91	3.65	1.41	1.13	17.9	3.28	49.4	7033	3
5/1	0	0.14	0.10	0.13	1.59	8.1	0.68	0.95	0.62	3.28	1.44	1.07	16.7	2.93	62.0	836	1
6	0	0.18	0.18	0.14	2.12	10.9	0.60	0.84	0.68	4.28	1.81	1.33	21.8	3.67	51.4	3493	1
10	0.29	0.38	0.58	1.04	6.00	44.4	1.12	0.89	0.98	5.28	1.56	1.44	12.0	1.13	22.8	834	2
7	0.12	0.19	0.21	0.18	2.57	13.1	0.76	1.09	0.88	4.23	2.12	1.62	23.2	2.89	46.8	1055	3
90	0	0	0	0	7.45	57.1	1.19	0.68	0.71	3.49	1.27	1.03	9.52	0.52	16.7	126	4
380	0.13	0.19	0.24	0.16	3.08	14.8	1.45	1.03	0.79	4.05	1.35	1.22	20.4	3.35	47.5	402	3
390	0	0	1.20	1.10	6.60	37.3	4.45	1.30	1.39	2.57	1.15	1.22	11.5	2.06	26.6	12.4	3
230	0.14	0.24	0.36	0.28	4.56	22.7	1.14	1.13	0.72	4.59	1.69	1.26	19.2	2.64	39.1	552	3
Caorle 2	0.20	0.17	0.69	0.65	8.95	62.1	0.76	1.12	0.63	1.13	0.90	1.66	6.8	0.83	13.3	47.6	5
Caorle 3	0	0	0.99	0.68	9.85	62.6	1.35	0.72	1.06	1.42	0.70	1.04	6.9	0.76	11.3	19.0	5
D2	0	0	0	0	3.55	17.2	1.11	1.64	1.13	4.84	1.63	1.52	26.1	1.85	39.0	140	2

Table 2. Eigenvalues, variance (%), and cumulative variance (%) associated to the four PC's selected (eigenvalue, >1.0).

Component number	*Eigenvalue*	*Percent of variance*	*Cumulative percentage*
1	6.39	39.97	39.97
2	4.47	27.93	67.90
3	1.57	9.79	77.69
4	1.28	8.00	85.69

Table 3. Sample scores.

Sample/Site	*Component 1*	*Component 2*	*Component 3*	*Component 4*
X1	-2.38	-3.17	-0.37	-1.42
E1	-1.74	-0.88	-0.49	-0.27
E2	-1.87	-1.19	-0.41	-0.43
E3	-1.58	-0.54	-0.50	-0.0062
E4	-1.17	0.66	-0.07	0.32
E5	-1.70	-3.17	-0.33	-0.11
E6	-1.12	1.19	-0.21	0.22
F1	-0.70	2.41	-0.10	0.21
F2	-1.54	2.03	-0.42	0.53
F3	0.47	4.76	-0.36	-0.52
F4	-1.26	1.82	-0.39	0.50
F5	0.25	4.59	0.09	0.22
Chioggia 1	3.14	-1.07	0.92	2.57
4	-1.08	-0.87	3.54	-1.50
5/1	-1.86	-2.14	0.06	-0.20
6	-2.58	-1.39	0.66	-0.72
10	2.49	1.87	-1.60	-2.12
7	-1.91	0.38	-0.16	0.37
90	2.95	-2.80	-1.65	1.66
380	-1.23	-0.59	0.13	-0.086
390	4.69	0.69	3.55	-0.51
230	-0.51	0.15	-0.58	-0.27
Caorle 2	5.04	-0.57	-1.91	-0.93
Caorle 3	6.22	-2.18	-0.067	-0.54
D2	-1.03	0.0058	0.69	3.02

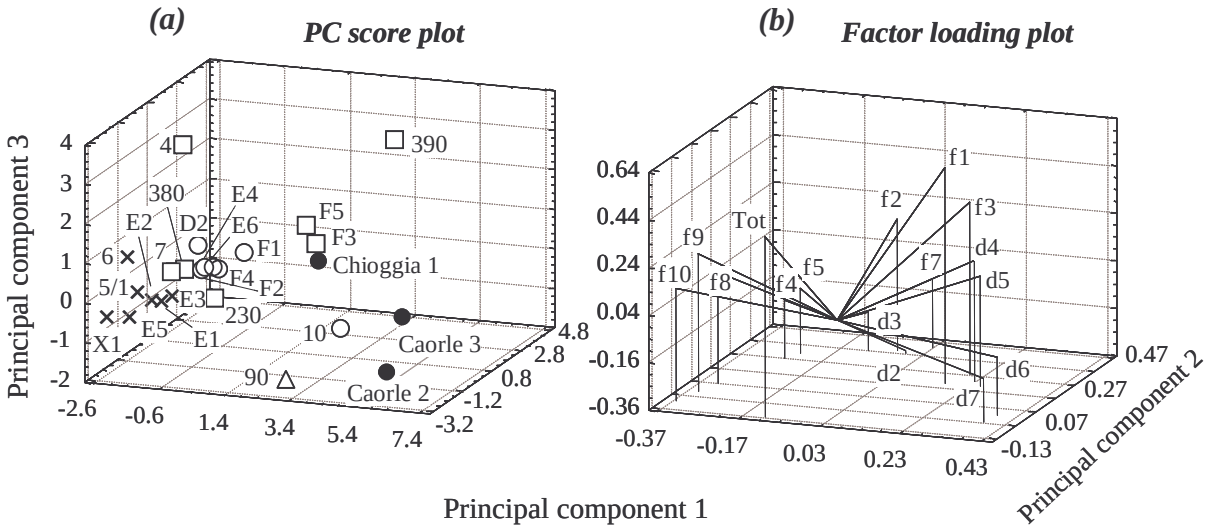

Figure 1. PCA score and factor loading plots obtained from PC's 1, 2, and 3 of the data set. The sample symbols (left view) reflect the subdivision in five virtual risk areas (cfr. Table 1): RA 1, ×; RA 2, ○; RA 3, □; RA 4, △; RA 5, ●.

d1, 2,3,7,8-T_4CDD; d2, 1,2,3,7,8-P_5CDD; d3, 1,2,3,4,7,8-H_6CDD; d4, 1,2,3,6,7,8-H_6CDD; d5, 1,2,3,7,8,9-

H_6CDD; d6, 1,2,3,4,6,7,8-H_7CDD; d7, O_8CDD; f1, 2,3,7,8-T_4CDF; f2, 1,2,3,7,8-P_5CDF; f3, 2,3,4,7,8-P_5CDF; f4, 1,2,3,4,7,8-H_6CDF; f5, 1,2,3,6,7,8-H_6CDF; f6, 1,2,3,7,8,9-H_6CDF; f7, 2,3,4,6,7,8-H_6CDF; f8, 1,2,3,4,6,7,8-H_7CDF; f9, 1,2,3,4,7,8,9-H_7CDF; f10, O_8CDF.

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