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

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Introduction

Since 1990, our laboratory has dealt with a number of field studies to characterize the chemical contamination of the Venice lagoon, with a focus on the assessment of a number of persistent organic pollutants (POPs) — such as the highly toxic polychlorinated dibenzodioxins (PCDDs), dibenzofurans (PCDFs), and biphenyls (PCBs) — and the development of human exposure scenarios thereof.[1] Over the last several years, studies have been carried out to investigate bottom sediments and clams *(Tapes sp.)* to develop strategies for risk management of local food production and contamination problems.[2] Within this framework, PCDD and PCDF profiles in clams collected at sediment sampling sites[3] have here been subjected to principal component analysis (PCA).

Materials and methods

Clam samples from Venice lagoon were collected (where available) in georeferenced sites, already sampled for sediments,[4] by professional operators. They were preliminarily classified according to the subdivision already adopted for the entire Venice lagoon,[1] subdivided into five virtual risk areas (RA's) with theoretically decreasing exposure values (Table 1) (a sixth RA was the sea neighbouring the lagoon). Once delivered to the laboratory, specimens were subjected to immediate pre-treatment: the matrices for analysis were pools (>200 g of fresh tissue) of the edible parts of many mollusc individuals. Pools were drained off to remove loose water. For the assessment of organic chemicals, matrices were stored at –20 °C; later, they were allowed to thaw out and combined with fully ^{13}C-labelled (internal) standards for chlorinated analytes. Quantitation of organic analytes was carried out by HRGC-LRMS(SIM) or -HRMS(SIM). Good laboratory practice and QA/QC protocols were applied throughout. Details on analytical procedure were reported elsewhere.[4] PCA was applied to PCDD and PCDF analytical data (Table 1). For each sample, congener concentrations were normalized against the pertinent cumulative analytical concentration Σ_{17}(PCDD+PCDF, pg/g), the latter obtained by the medium bound approach when dealing with limits of determination. Samples (cases) and congeners (variables) with a high incidence (>40 %) of non-detects throughout the samples were removed to minimize the non-detect impact on PCA.[5]

Results and discussion

Three components were extracted from the data set, that accounted for a cumulative percentage of 85 % (Table 2). The first component (PC 1) weighs more in the positive direction for the samples collected in background areas, and in the negative direction for samples from sites under industrial impact(s) (Table 3; Figure 1): among the principal factors influencing sample distribution densities in the Venice lagoon,[5] it has a particular discriminating power. From the factor loadings plot (Figure 1), d6 and d7 are the variables with the highest positive loadings whereas those with the highest negative loadings are f4, f5, f8, f9, and f10. These two congener patterns appear to reflect, respectively, a generic combustion origin followed by atmospheric fallout and the release from industrial sources once present in the industrial area of Porto Marghera. PC 2, whose highest positive loadings are associated with variables f1, f2, f3, and f6, has the maximum scores for samples 4411, 4410, 7473, and 7474 (Figure 1). These samples were obtained from the Canal Grande in Venice and from the main Chioggia Canal, two areas exposed essentially to motorboat traffic. In PC 2, the highest negative scores are for samples collected in industrial and background areas. This congener profile seems to represent in clams an "urban type" feature and the differences from the profile with a similar classification for sediments could be ascribed to the toxicokinetic and toxicodynamic processes in the organism. As already observed for sediments,[3] the data set in Table 1 may be subdivided into three clusters according to the pertinent local exposures. Therefore, clams appear to reflect local pollution as well, and the five risk areas hypothesized (Table 1) can be reduced to three.

References

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

Sample/Site	*d4*	*d6*	*d7*	*f1*	*f2*	*f3*	*f4*	*f5*	*f7*	*f8*	*f9*	*f10*	*Total*	*RA*
X1	0.38	2.42	10.7	3.07	1.81	1.49	5.26	2.39	2.25	22.1	3.05	44.1	32.1	1
E3	0	4.76	6.7	9.52	2.94	3.90	5.63	2.77	3.12	22.5	2.08	32.9	11.6	1
E4	0	4.01	20.1	7.12	2.55	2.74	4.38	2.19	1.64	18.2	2.01	31.9	11.0	2
E5	0.38	3.23	12.0	5.96	2.08	2.82	5.28	2.40	2.88	23.9	2.71	35.3	20.0	1
E6	0	3.72	15.4	8.89	3.64	3.23	6.14	3.31	2.34	20.2	2.43	28.3	12.4	2
F2	2.05	7.08	20.5	14.2	3.72	4.84	4.47	0	2.61	14.5	0	18.1	5.37	2
F4	0.50	4.27	14.2	11.5	2.47	3.05	5.62	3.11	3.73	25.2	2.19	22.7	8.49	2
5/2	0.34	2.18	9.2	5.88	1.97	2.32	5.42	2.60	2.49	17.2	2.14	47.1	31.6	1
7484	0.24	1.81	7.9	4.64	1.66	1.69	5.08	2.18	1.89	16.1	3.22	51.5	42.0	1
4411	0.33	3.35	13.1	22.0	3.47	5.72	4.89	2.17	3.21	17.7	2.03	20.3	12.6	2
4410	0.45	3.90	13.9	24.2	3.79	4.89	4.60	2.41	3.65	16.4	1.71	18.0	7.77	3
7C	0.50	3.14	12.2	8.04	2.14	2.99	6.29	2.87	3.30	19.0	2.49	35.6	15.2	3
8/2	0	3.51	12.7	6.72	1.93	2.65	5.35	2.61	3.16	19.2	2.41	36.1	8.75	3
7483	0.41	2.72	9.4	12.5	2.81	3.66	5.52	3.00	3.22	21.4	2.92	29.8	25.9	3
7473	0.46	4.80	24.4	38.5	2.87	6.09	2.88	1.40	2.18	8.23	0.55	5.73	3.17	3
7474	0.56	4.03	15.3	36.8	2.87	6.35	4.14	2.37	3.64	10.4	1.12	10.5	4.49	3
7475	0	6.34	28.4	17.0	2.24	2.73	3.04	1.91	2.37	7.35	0	23.2	1.40	4
Chioggia 90	0.61	9.03	44.9	10.5	1.85	3.43	2.46	1.23	2.05	11.4	0.93	10.1	2.48	5
Scardovari	0.67	9.46	60.0	7.09	1.57	2.93	1.64	0.94	1.31	6.08	0.39	6.74	3.09	5
Caleri	0.61	10.9	63.5	5.42	1.34	2.14	2.17	1.00	1.18	5.59	0.47	4.87	3.43	5
D2	0.44	4.02	17.3	16.3	2.82	4.77	5.44	2.24	3.31	18.6	2.07	21.3	4.46	3
Pel 1	0.45	5.74	21.4	8.36	2.03	3.44	4.59	1.88	3.05	20.6	2.43	24.6	2.52	5
S. Erasmo	0	5.57	18.4	16.5	2.66	5.58	4.29	2.62	3.68	18.3	1.74	18.7	1.74	5

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

Component number	*Eigenvalue*	*Percent of variance*	*Cumulative percentage*
1	6.52	50.17	50.17
2	3.38	25.98	76.15
3	1.20	9.25	85.40

Table 3. Sample scores.

Samples/Site	*Component 1*	*Component 2*	*Component 3*
X1	-2.78	-2.39	0.74
E3	-1.85	0.60	-0.50
E4	-0.48	-1.25	-0.51
E5	-2.14	-0.89	0.37
E6	-1.98	0.41	-0.60
F2	3.08	1.57	4.32
F4	-1.70	0.69	-0.17
5/2	-2.40	-1.67	0.56
7484	-2.85	-2.92	0.77
4411	-0.49	2.28	0.070
4410	-0.15	2.66	0.0087
7C	-2.16	-0.25	0.23
8/2	-1.77	-0.71	-0.84
7483	-2.49	0.43	0.27
7473	3.15	2.33	-0.45
7474	1.27	3.34	-0.54
7475	2.35	-0.54	-1.32
Chioggia 90	3.61	-1.22	-0.22
Scardovari	5.09	-2.38	-0.27
Caleri	5.19	-3.02	-0.46
D2	-0.46	1.46	-0.024
Pel 1	-0.089	-0.29	-0.073
S. Erasmo	0.046	1.76	-1.39

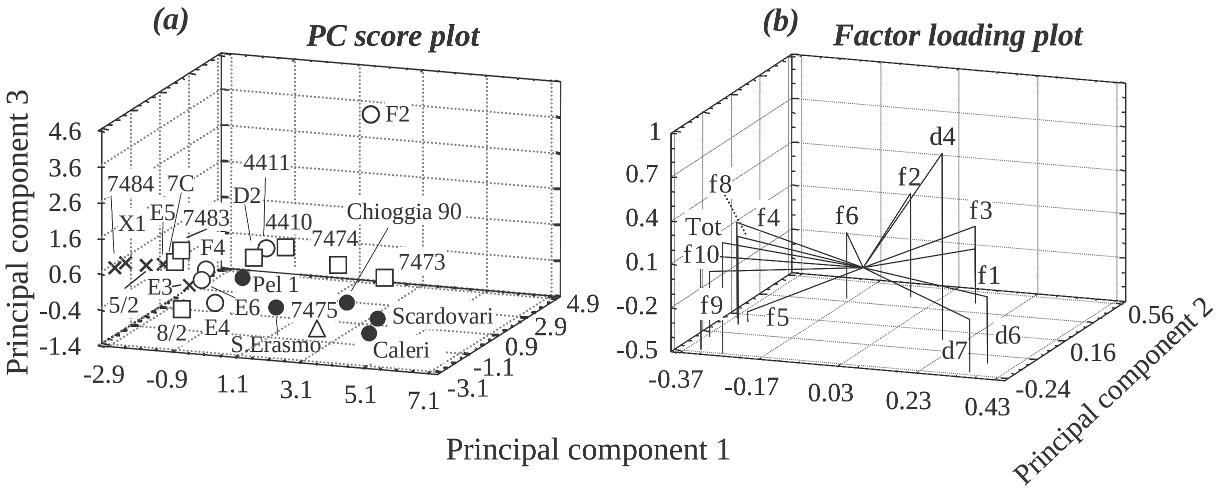

Figure 1. PCA score– (a) and factor loading (b) plots obtained from PC's 1, 2 and 3 of the data set. The sample symbols in the main box reflect the subdivision in five virtual risk areas (cfr. Table 1): RA 1, ×; RA 2, ○; RA 3, □; RA 4, △; RA 5, ●.

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.