Correlation between PCDD and PCDF Levels in Sediments and Clams (*Tapes sp.*) in the Venice Lagoon

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Introduction

Since the early '90s, our laboratory has dealt with field studies to characterize the persistent chemical contamination in the Venice lagoon and the associated toxicological risks for residents. In 2000, financial support from the Veneto Region was obtained to define strategies for appropriate risk management of food produced in the lagoon and potentially exposed to highly toxic PCDDs and PCDFs, whose concentrations in bottom sediments may be remarkably higher than background.[1] Clam (*Tapes sp.*) cultivation is a typical traditional and remunerative economic activity that has recently been regulated by the Regional Authority. This has resulted in expanding cultivation to central lagoon sections, once contained in a wide area surrounding the city of Venice, prohibited to food production for hygienic and safety reasons. However, sections were allowed to clam cultivation with some restrictions.

In 2000, a preliminary study was carried out to compare the PCDD and PCDF levels measured by previous investigations in congruent specimens of clams and bottom sediments.[2] As the number of data available from *ad hoc* assessments has considerably grown, an update of the former study has been undertaken. Its results are summarized hereafter.

Experimental and modeling

Data were derived from unpublished and published material.[1–4] The 20 pairs of PCDD+PCDF concentration values selected — X, in dry sediments; Y, in whole clams — were obtained from samplings performed in 1992, 1995, 1998, and 2000 in different lagoon zones/sites (see table; Figure 1). Paired X-Y values were selected when the congruent sampling zones/sites were under a reasonably even and well-characterized local impact, a condition strictly verified for the *ad hoc* samplings of 1998 and 2000. Otherwise, X and Y samplings were consistent with the same virtual risk area,[1] i.e. they were associated with zones/sites relatively close to one another.

Linear regressions were carried out with the canonical form $y = w\,x + q$ (*Eqn*. 1) on the sets of 20 ln-transformed analytical and international TE X-Y values, where: $y = \ln(Y)$; $x = \ln(X)$; $q = \ln(m)$.[2] In a linear field, *Eqn*. 1 reverts to the (parabolic) power function $Y = m\,X^w$ (*Eqn*. 2). The simplest bioaccumulation model is $C_{TSS} = BAF\ C_S$ (*Eqn*. 3), where: C_{TSS}, tissue concentration at steady state; C_S, sediment concentration; BAF, bioaccumulation factor.[5] For $w = 1$, *Eqns*. 2 and 3 formally coincide, with $Y \equiv C_{TSS}$, $X \equiv C_S$, and $m \equiv BAF$.

Sediment and clam sample identification codes, and pertinent concentration levels expressed in analytical units (pg/g) and as international 2,3,7,8-T_4CDD equivalents (I-TE units).

SAMPLE ID [a]		**PCDDs+PCDFs (*pg/g*)** [b]		**PCDDs+PCDFs (*pgI-TE/g*)** [b]	
Sediment	***Clam***	***Sediments***	***Clams***	***Sediments***	***Clams***
E1-S	E1-B	930	12	15	0.60
E2-S	E2-B	810	3.8	13	0.43
E3-S	E3-B	84	12	1.4	0.63
E4-S	E4-B	76	11	1.6	0.46
E5-S	E5-B	120	15	1.6	0.69
E5-S	E5-B	120	20	1.6	0.78
E6-S	E6-B	150	12	3.1	0.61
F2-S	F2-B	150	5.4	3.4	0.38
F3-S	F3-B	29	6.9	0.77	0.39
F4-S	F4-B	320	9.0	6.7	0.49
F4-S	F4-B	320	8.5	6.7	0.42
Chioggia 1-S	Chioggia 1-B	9.0	2.9	0.24	0.17
X1-S	X1-B	2500	32	29	0.87
S-380	B-480	400	16	7.2	0.42
90	7473, 7474	130	3.8 [c]	1.8	0.33 [c]
10	4411	840	13	18	0.87
7A	7B, 7483	1300	19 [c]	24	1.0 [c]
40	12*, 14*	1400	18 [c]	23	1.1 [c]
4A, 5/1A	5/2B, 8*	3600 [c]	32 [c]	48 [c]	1.4 [c]
6A	7484, 9*	3900	25 [c]	56	1.1 [c]

(a) ID codes were reported to match original References 1, 2, and 4. *(b)* Dry and whole (fresh) weight for sediments and clams, respectively. Rounding-off to two figures. *(c)* Mean values.

Results and discussion

Figure 2 exhibits the ln-transformed analytical and I-TE data scattergraphs, *Eqn*. 1 best fit lines, and the related regression equations, both highly significant. The level of significance is higher for the I-TE data set: this suggests that conversion to TEQs determine a relative overweighting of the values of those congeners that are likely quantitated with a higher level of accuracy/precision.

Based on regression coefficients and their standard errors in *Eqns*. 1, *Eqn*. 2 may be written as $Y = (2.3 \pm \approx 1.0)\ X^{(0.280 \pm 0.075)}$ (*Eqn*. 2a) and $Y = (0.373 \pm \approx 0.044)\ X^{(0.263 \pm 0.053)}$ (*Eqn*. 2b), for analytical and I-TE data, respectively. These are clearly non-linear relationships ($w \neq 1$): in particular, the rate of Y increase diminishes with increasing X ($w < 1$). In other words, as shown previously,[2] and in agreement with environmental observations,[5,6] the bioaccumulation process rate described by *Eqns*. 2a and 2b is greater at lower environmental concentrations than at the higher ones. As predictable, *Eqns*. 2a and 2b intersect the *Eqn*. 3 linear bioaccumulation models obtained from regressions on the same data sets, and yield Y estimates in reasonable agreement over the following X values (intersection, range): 2000, 1600–2400 pg/g; 30, 24–36 pgI-TE/g.

Figure 3 exhibits the analytical and I-TE data scattergraphs in an X-Y linear field, *Eqn*. 2 best fit lines, and the related non-linear regression equations $Y = (1.79 \pm 0.91)\ X^{(0.330 \pm 0.071)}$ (*Eqn*. 2c) and $Y = (0.363 \pm 0.060)\ X^{(0.291 \pm 0.055)}$ (*Eqn*. 2d). Again, fitting improves for the I-TE data set.

The patterns of *Eqns*. 2c and 2d, undistinguishable from *Eqns*. 2a and 2b, clearly show the non-linear trends of $[PCDDs+PCDFs]_{CLAMS}$ *vs*. $[PCDDs+PCDFs]_{SEDIMENTS}$.

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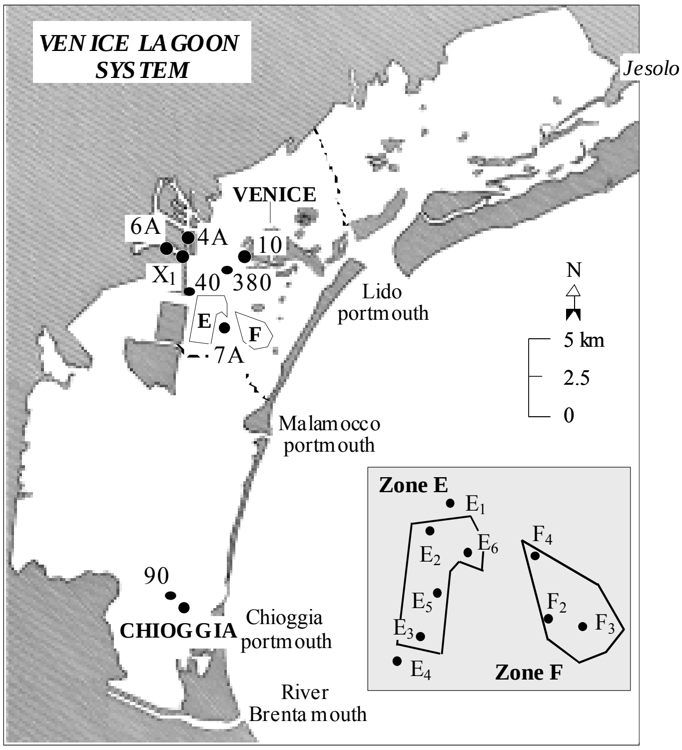

Figure 3. Sediment sampling sites. Clam samplings, not shown, were performed at corresponding sites (see table). The area within the two dashed lines is under health restrictions. Sampling locations in Zones E and F are visible in the enlargement.

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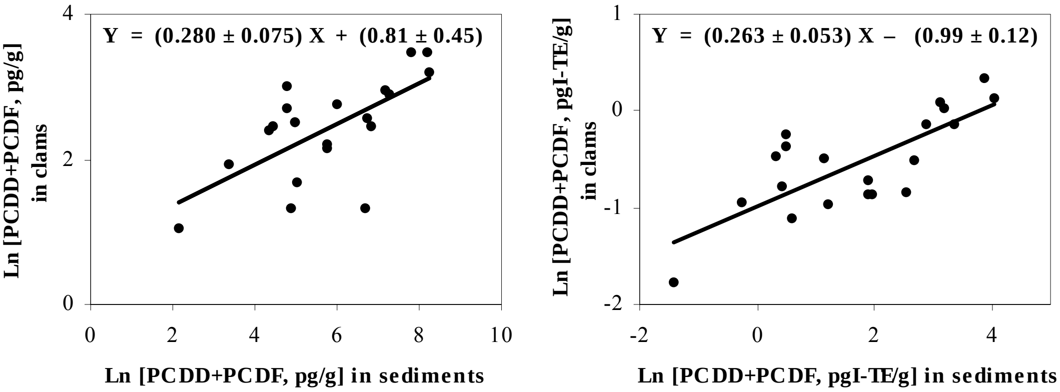

Figure 2. Correlations between ln-transformed PCDD+PCDF concentration values in clams and bottom sediments from the Venice lagoon. Linear regressions were carried out on the analytical (left; R = 0.660, P_R < 0.01; $F_{1,18}$ = 13.9, P_F < 0.01) and I-TE (right; R = 0.759, P_R < 0.001; $F_{1,18}$ = 24.5, P_F < 0.001) data sets.

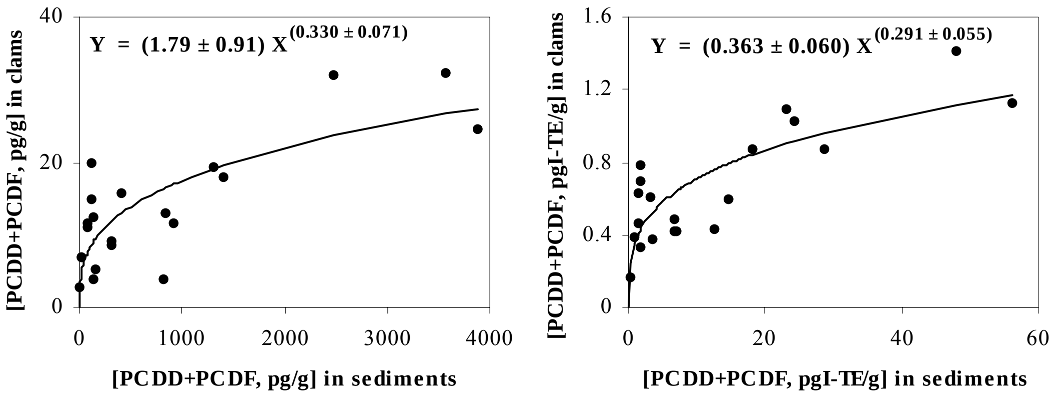

Figure 3. Correlations between PCDD+PCDF concentration values in clams and bottom sediments from the Venice lagoon. Non-linear regressions were carried out on the analytical (left; R^2 = 0.575) and I-TE (right; R^2 = 0.633) data sets.