# Persistent and toxic substances in the Venice lagoon biota: an approach for quantitative data analysis for risk management

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**Summary.** An approach based on hypothesis testing for the management of persistent inorganic and organic toxic chemicals (PTS/POPs) detected in clams and mussels from the Venice lagoon is presented. The chemicals of interest for this evaluation were the polychlorinated biphenyls (PCBs), dibenzodioxins (PCDDs), and dibenzofurans (PCDFs), hexachlorobenzene (HCB), and the heavy metals cadmium (Cd), mercury (Hg), and lead (Pb). Two statistically different populations of data for PCDDs+PCDFs (TEQs), HCB, Cd, and Pb, associated with biota samples collected respectively in the lagoon central district and in the southern and northern districts were identified. The central district is under the impact of the Porto Marghera industrial settlement and the city of Venice, whereas the southern and northern districts are subject to a general impact. Of the aforementioned chemicals, those with more discriminating power were found to be HCB and PCDDs+PCDFs.

Key words: Venice lagoon, hypothesis testing, risk management, biota.

**Riassunto** (Sostanze tossiche e persistenti in organismi della Laguna di Venezia: un approccio per l'analisi quantitativa dei dati per la gestione del rischio). Viene presentato un approccio per il management dei livelli di contaminanti persistenti organici e inorganici nei tessuti di bivalvi campionati nella laguna di Venezia. Le sostanze chimiche d'interesse, selezionate sulla base di dati ambientali locali e la loro rilevanza tossicologica, sono i bifenili (PCB), le dibenzodiossine (PCDD), e i dibenzofurani (PCDF) policlorurati, l'esaclorobenzene (HCB), e i metalli pesanti cadmio (Cd), mercurio (Hg), e piombo (Pb). L'approccio ha consentito di identificare con chiarezza due popolazioni statisticamente diverse per i valori di PCDD+PCDF (TEQ), HCB, Cd, e Pb associati con campioni prelevati rispettivamente, nel bacino centrale e in quelli meridionale/settentrionale. Il distretto centrale è sotto l'impatto dell'area industriale di Porto Marghera e della città di Venezia, mentre gli altri due sembrano essere sotto un impatto di tipo generale. Le sostanze chimiche con più potere discriminativo sono state HCB e PCDD+PCDF.

Parole chiave: laguna di Venezia, saggio delle ipotesi, gestione del rischio, biota.

## **INTRODUCTION**

A comprehensive risk management for the contaminants present in bottom sediments of the Venice lagoon appears to be complicated by three issues: the past, present, and future influence of human pressure; the obvious sensitivity of a wetland like the lagoon; its extension. The actual situation can be viewed as typical of stressors at regional scale [1, 2].

The relationships between a coastal city and its environment are one of the central question addressed in Chapter 17 of Agenda 21, adopted at the United Nations Conference on Environment and Development (UNCED) [3]. In this chapter, the importance of coasts in a life-supporting system and the positive opportunity for sustainable development that coastal areas represent are stressed. However, in industrialized countries a practicable co-existence of environment and development will require mostly regulatory measures to regulate their relationships.

The Venice lagoon is one of the leading shellfish production areas in Italy, harvesting thousands metric tons per year of the clam *Tapes philippinarum* and the mussel *Mytilus galloprovincialis*. A number of studies in recent years have characterized the chemical contamination of matrices like biota and sediment. The chemicals analyzed belong to different families including organic contaminants such as polychlorinated dibenzodioxins (PCDDs) and dibenzofurans (PCDFs), chlorinated pesticides, heavy metals, organometals, etc. The primary contamination sources have been clearly identified with Porto Marghera industrial settlement and the city of Venice with its canals, motorboats, and dense anthropogenic activity: the impacts of these activities

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appear to be concentrated in the central district (*Figure 1*). This impact pattern was observed by several authors. The heavy metals concentrations found in the industrial canals are presently the most likely source of toxic metals to the lagoon [4], whereas a spatial decreasing of pollution levels was also detected for organic microcontaminants when moving from the industrial zone to lagoon areas closer to the sea [5, 6]. Indeed, in our studies on the lagoon environment, the following four impact types were identified: industrial, urban, "not classifiable", and lagoon background [7-11].

In this paper, the polychlorobiphenyls (non-dioxin-like PCB congeners), PCDD+PCDF, hexachlorobenzene (HCB), cadmium (Cd), mercury (Hg), and lead (Pb) levels found in organisms collected in the central district of the lagoon, overexposed to the primary impacts and forbidden to fishing, are compared with those of specimens collected in the other two districts within the lagoon (*Figure 1*). Thereby, a quantitative description of contaminant presence in the lagoon is provided by an empirical approach based on hypothesis testing that appears to be suitable for regional scale impact management [1, 2]. In addition, the statistics obtained have been evaluated against the maximum acceptance levels (MLs) provided by international regulation on fish and fishery products [12, 13].

## MATERIALS AND METHODS

In recent years, edible biota from the central and other lagoon areas was analyzed for its persistent organic and



**Fig. 1** | Layout of the Venice lagoon area showing the three districts functional to this study. The central district includes the Porto Marghera industrial settlement, the city of Venice, and a part of the Malamocco-Marghera industrial channel. The entire lagoon area covers some 550 km<sup>2</sup>.

inorganic toxic chemical (PTS) contents in research and monitoring programs: specimens were collected in situ between 1995 and 2002 [14, 15], and included shellfish such as clams (Tapes sp.) and mussels (Mytilus galloprovincialis) [8, 9, 15]. In parallel studies on lagoon sediments, sampling site or zone classification, based on presumed local impact(s), was developed [7, 10, 11]: in conformity, the biota data dealt with in this analysis were grouped into specimens from the central district, under industrial and/or urban impact, and specimens from the northern and southern districts, under a general and/or aspecific ("not classifiable" and lagoon background) impact. The clams/mussels ratios in the two groups ranged 0.8-1.4. This variation is due to the samples availability for chemical-specific determinations. In this work, the levels of PCBs (as the sum of the six canonical non-dioxin-like indicator congeners [16]), PCDDs+PCDFs (TEQs), HCB, Cd, Hg, and Pb were considered, as in the outcome of sediment analysis they appeared to be both, more sensitive of all the chemical pollution markers studied by our group to investigate the Venice lagoon contamination and more interesting from a toxicological point of view.

Bivalves matrices for analysis were obtained by aggregating > 200 g fresh matrix of the edible parts of many molluscs of the same type collected at a given site and of approximately the same size. Each frozen specimen was allowed to thaw out in the laboratory and rinsed externally with abundant distilled water; the edible parts were then thoroughly excised from the opened mollusc after careful rinsing of the inside with more distilled water to remove sand/sediment or impurities. The excised parts were combined together, gently deprived of excess water, extensively homogenized to yield the matrix for analysis, and stored again at -20 °C in a plastic bag for food use in view of analytical processing. Before it, for the assessment of organic chemicals the analytical samples were allowed to thaw out, then spiked with fully <sup>13</sup>C-labelled standards, gently homogenized and, after the canonical clean-up steps, quantified by high-resolution gas chromatography coupled with low- or high-resolution mass spectrometry (HRGC-LRMS or -HRMS) used in the selected ion monitoring (SIM) mode. Details on the analytical procedure as well as on GLP and QA/QC protocols are reported elsewhere [7-10, 17]. In general, internal standards were recovered with medium-to-high mean yields (> 40%); low recovery yields were not considered to be adequate and the analysis was repeated.

Heavy metals were measured by AAS techniques after acid digestion of fresh tissue samples collected from the available homogenates [17-19].

The data of interest – whose values for each analyte are ranked low to high – are summarized in *Table 1* for the northern and southern districts together, and in *Table 2* for the central district. Chemical-specific databases differ because the research and monitoring programs where data were acquired dealt with a range of different objectives. PCDD+PCDF data in *Tables 1, 2,* and *3* and in *Figure 2* are expressed in equivalents of toxicity of 2,3,7,8-TCDD (TEQs), after converting the original congener analytical data with the International (I) and the World Health Organization (WHO) TEFs Table 1 | PCB, PCDD+PCDF, HCB, Cd, Hg, and Pb concentrations on a fresh weight base in clam and mussel samples collected from the northern and southern districts of the Venice lagoon. Samplings carried out between 1995 and 2002

| Entry  | Concentration levels a |       |          |          |        |        |         |  |  |
|--------|------------------------|-------|----------|----------|--------|--------|---------|--|--|
| number | PCBs <sup>b</sup>      |       | -PCDFs ° | HCB      | Cd     | Hg     | Pb      |  |  |
|        | <i>ng g</i> ⁻¹         | pg1   | 'E g⁻¹   | ng g⁻¹   | µg g⁻¹ | µg g⁻¹ | µg g⁻¹  |  |  |
| 1      | 0.65                   | 0.064 | 0.065    | <0.005 d | 0.0020 | 0.0035 | ≈0.01 e |  |  |
| 2      | 1.9                    | 0.067 | 0.068    | 0.018    | 0.0070 | 0.011  | ≈0.03   |  |  |
| 3      | 2.5                    | 0.083 | 0.079    | 0.019    | 0.029  | 0.016  | 0.11    |  |  |
| 4      | 3.1                    | 0.087 | 0.084    | 0.022    | 0.031  | 0.027  | 0.13    |  |  |
| 5      | 3.1                    | 0.090 | 0.091    | 0.023    | 0.032  | 0.028  | 0.13    |  |  |
| 6      | 3.2                    | 0.12  | ≈0.1     | 0.031    | 0.032  | 0.029  | 0.16    |  |  |
| 7      | 3.3                    | 0.16  | ≈0.1     | 0.034    | 0.036  | 0.030  | 0.16    |  |  |
| 8      | 3.3                    | ≈0.2  | ≈0.1     | 0.040    | 0.037  | 0.032  | 0.16    |  |  |
| 9      | 4.9                    | ≈0.2  | 0.12     | 0.048    | 0.060  | 0.033  | 0.17    |  |  |
| 10     | 5.0                    | ≈0.2  | 0.15     | 0.062    | 0.082  | 0.034  | 0.19    |  |  |
| 11     | 5.7                    | ≈0.2  | ≈0.2     | <0.08    | 0.12   | 0.034  | 0.20    |  |  |
| 12     | 5.8                    | ≈0.2  | ≈0.2     | 0.11     | 0.13   | 0.039  | 0.20    |  |  |
| 13     | 6.5                    | ≈0.2  | ≈0.2     | 0.11     | 0.13   | 0.040  | 0.23    |  |  |
| 14     | 6.7                    | ≈0.2  | ≈0.2     | 0.12     | 0.13   | 0.042  | 0.24    |  |  |
| 15     | 6.8                    | ≈0.2  | ≈0.2     | 0.12     | 0.14   | 0.045  | 0.24    |  |  |
| 16     | 7.7                    | 0.24  | ≈0.2     | 0.14     | 0.14   | 0.056  | 0.42    |  |  |
| 17     | 9.1                    | 0.25  | 0.23     | 0.17     | 0.14   | 0.057  |         |  |  |
| 18     | 9.1                    | 0.28  | 0.24     | 0.17     | 0.16   | 0.058  |         |  |  |
| 19     | 12                     | ≈0.3  | 0.27     | 0.19     | 0.17   | 0.059  |         |  |  |
| 20     | 13                     | 0.31  | 0.30     | 0.23     | 0.17   | 0.061  |         |  |  |
| 21     | 14                     | 0.31  | 0.31     | 0.28     | 0.17   | 0.063  |         |  |  |
| 22     | 14                     | 0.32  | 0.31     | 0.29     | 0.18   | 0.081  |         |  |  |
| 23     | 14                     | 0.33  | 0.32     | 0.44     | 0.19   | 0.098  |         |  |  |
| 24     | 15                     | 0.35  | 0.33     | 0.50     | 0.21   | 0.12   |         |  |  |
| 25     | 15                     | 0.37  | 0.36     | 0.55     | 0.31   | 0.24   |         |  |  |
| 26     | 17                     | 0.38  | 0.37     | 0.60     | 0.34   | 0.25   |         |  |  |
| 27     | 19                     | 0.38  | 0.38     | 0.83     | 0.43   | 0.36   |         |  |  |
| 28     | 21                     | 0.39  | 0.39     |          | 0.60   | 0.48   |         |  |  |
| 29     |                        | 0.41  | 0.40     |          |        |        |         |  |  |
| 30     |                        | 0.43  | 0.42     |          |        |        |         |  |  |
| 31     |                        | 0.45  | 0.44     |          |        |        |         |  |  |
| 32     |                        | 0.46  | 0.46     |          |        |        |         |  |  |
| 33     |                        | 0.48  | 0.47     |          |        |        |         |  |  |
| 34     |                        | 0.51  | 0.49     |          |        |        |         |  |  |
| 35     |                        | 0.53  | 0.52     |          |        |        |         |  |  |
| 36     |                        | 0.55  | 0.54     |          |        |        |         |  |  |
| 37     |                        | 0.57  | 0.57     |          |        |        |         |  |  |
| 38     |                        | 0.64  | 0.63     |          |        |        |         |  |  |
| 39     |                        | 0.69  | 0.68     |          |        |        |         |  |  |
| 40     |                        | 1.5   | 1.3      |          |        |        |         |  |  |

<sup>(a)</sup>Estimated average uncertainty on measurements,  $\leq |\pm 10\%|$ . Values rounded off to two figures.

<sup>(b)</sup>Σ6(PCBs) = [PCB-28] + [PCB-52] + [PCB-101] + [PCB-138] + [PCB-153] + [PCB-180]. <sup>(c)</sup>Left column: WHO-TEQs. Right column: I-TEQs.

<sup>(d)</sup>The sign  $\leq$  indicates limit of quantification ( $\leq$ LOQ).

 $^{(e)}$ Figures preceded by  $\approx$  are "not representative" as they include many congeners below limit of quantification (<LOQ).

**Table 2** | *PCB*, *PCDD*+*PCDF*, *HCB*, *Cd*, *Hg*, and *Pb* concentrations on a fresh weight base in clam and mussel samples from the central district of the Venice lagoon. Samplings carried out between 1995 and 2002

| Entry  | Concentration levels <sup>a</sup> |        |                   |                           |        |                     |        |  |  |
|--------|-----------------------------------|--------|-------------------|---------------------------|--------|---------------------|--------|--|--|
| number | PCBs <sup>b</sup>                 | PCDDs+ | -PCDFs °          | HCB                       | Cd     | Hg                  | Pb     |  |  |
|        | ng g⁻¹                            | pgT    | E g <sup>−1</sup> | <b>ng g</b> <sup>-1</sup> | µg g⁻¹ | µg g <sup>−1</sup>  | µg g⁻¹ |  |  |
| 1      | 1.4                               | 0.20   | 0.17              | 0.084                     | 0.14   | 0.0056              | 0.063  |  |  |
| 2      | 1.4                               | 0.33   | 0.31              | 0.37                      | 0.15   | 0.0082              | 0.24   |  |  |
| 3      | 1.6                               | 0.40   | 0.38              | 0.38                      | 0.17   | 0.041               | 0.24   |  |  |
| 4      | 2.1                               | 0.41   | 0.39              | 0.48                      | 0.18   | 0.042               | 0.25   |  |  |
| 5      | 2.5                               | 0.43   | 0.41              | 0.53                      | 0.22   | 0.045               | 0.28   |  |  |
| 6      | 2.7                               | 0.44   | 0.42              | 0.54                      | 0.24   | < 0.05 <sup>d</sup> | 0.33   |  |  |
| 7      | 3.0                               | 0.45   | 0.42              | 0.59                      | 0.26   | < 0.05              | 0.37   |  |  |
| 8      | 3.4                               | 0.46   | 0.43              | 0.73                      | 0.27   | < 0.05              | 0.44   |  |  |
| 9      | 3.4                               | 0.48   | 0.46              | 1.5                       | 0.30   | < 0.05              | 0.44   |  |  |
| 10     | 4.5                               | 0.54   | 0.52              | 1.5                       | 0.38   | 0.053               | 0.45   |  |  |
| 11     | 4.5                               | 0.62   | 0.54              | 1.7                       | 0.40   | 0.055               | 0.46   |  |  |
| 12     | 4.8                               | 0.63   | 0.60              | 2.5                       | 0.41   | 0.061               | 0.46   |  |  |
| 13     | 6.1                               | 0.65   | 0.61              | 2.7                       | 0.42   | 0.074               | <0.5   |  |  |
| 14     | 7.2                               | 0.73   | 0.63              | 4.0                       | 0.45   | 0.076               | 0.69   |  |  |
| 15     | 8.8                               | 0.80   | 0.72              | 4.8                       | 0.48   | 0.076               | 0.78   |  |  |
| 16     | 9.8                               | 0.88   | 0.78              | 7.8                       | <0.5   | 0.082               | 0.79   |  |  |
| 17     | 10                                | 0.88   | 0.78              | 8.4                       | <0.5   | 0.12                | 1.09   |  |  |
| 18     | 10                                | 1.1    | 0.87              | 9.4                       | 0.75   | 0.13                |        |  |  |
| 19     | 11                                | 1.2    | 0.87              | 13                        | 0.97   | 0.14                |        |  |  |
| 20     | 43                                | 1.3    | 0.91              | 18                        | 1.4    | 0.15                |        |  |  |
| 21     | 51                                | 1.4    | 0.98              |                           |        |                     |        |  |  |
| 22     | 67                                | 1.7    | 1.1               |                           |        |                     |        |  |  |
| 23     | 88                                | 1.9    | 1.2               |                           |        |                     |        |  |  |
| 24     |                                   | 5.4    | 1.3               |                           |        |                     |        |  |  |
| 25     |                                   |        | 1.3               |                           |        |                     |        |  |  |
| 26     |                                   |        | 1.4               |                           |        |                     |        |  |  |
| 27     |                                   |        | 1.5               |                           |        |                     |        |  |  |
| 28     |                                   |        | 1.6               |                           |        |                     |        |  |  |
| 29     |                                   |        | 1.8               |                           |        |                     |        |  |  |
| 30     |                                   |        | 1.9               |                           |        |                     |        |  |  |
| 31     |                                   |        | 2.7               |                           |        |                     |        |  |  |
| 32     |                                   |        | 5.3               |                           |        |                     |        |  |  |

"Estimated average uncertainty on measurements,  $\leq |\pm 10\%|$ . Values rounded off to two figures

 ${}^{(b)}\Sigma6(PCBs) = [PCB-28] + [PCB-52] + [PCB-101] + [PCB-138] + [PCB-153] + [PCB-180].$ 

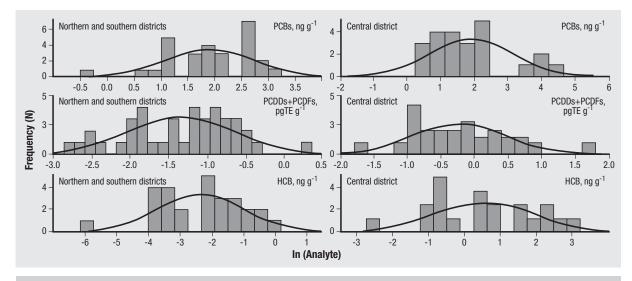
<sup>(e)</sup>Left column: WHO-TEQs. Right column: I-TEQs.

 $^{(d)}$ *The sign* < *indicates limit of quantification* (<*LOQ*).

systems [20, 21]. In the PCDD+PCDF frequency distributions shown in *Figure 2*, only the data converted with the WHO-TEFs system are presented.

To obtain normal distributions, the original values (*Table 1* and *Table 2*) underwent logarithmic or square-root (for Cd and Pb data) transformation; undetermined results (< LOQ) were entered in calculations as "LOQ  $\times$  0.5". The transformed data sets were subjected to descriptive statistics and Kolmogorov-Smirnov's and Shapiro-Wilks' *W* normality tests (*P* = 0.05). Hypothesis testing was adopted to assess whether, for each chemical, the two data distributions available were significantly different [1]: for the null

 $(H_0)$  hypothesis, no difference was expected to be detected between the means of the two transformed data sets, H1 being the alternative one. The meaning of these two hierarchical hypotheses consisted in detecting whether a statistical difference existed between sample results grouped as described above and, if affirmative, in linking results to sampling sites to define spatial impacts. The two-sided Student's t-test was used to discriminate whether the two sets of data available for each chemical were significantly (P = 0.05) different. In addition, this procedure allowed to select the chemicals with the best discriminatory power among those analyzed.

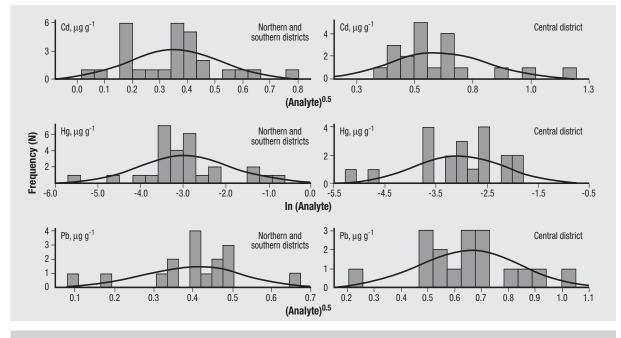


**Fig. 2** | *PCB*, *PCDD*+*PCDF*, and *HCB* concentration distributions in clams and mussels from the Venice lagoon northern and southern (left boxes) and central (right boxes) districts, according to the data summarized in Tables 1 and 2. To deal with normal distributions, the original data – expressed on a fresh weight base in ng g<sup>-1</sup> for PCBs and HCB, and in pgI-TE g<sup>-1</sup> for PCDDs+PCDFs – were converted to natural logarithms (ln[x]), as shown in the figure.

### **RESULTS AND DISCUSSION**

The plots of the transformed data sets for the chemicals dealt with in this analysis are shown in *Figure 2* (organochlorine compounds) and *Figure 3* (heavy metals) as normal frequency distribution curves superimposed to histograms. Some statistics of the distributions of interest are summarized in *Table 3* (organochlorine compounds) and *Table 4* (heavy metals), after conversion to the original linear co-ordinates.

Although on a chemical-specific base there are evident distribution overlapping – as elicited from  $X_{MN}$ – $X_{MAX}$  and percentile  $(Q_{.10} - Q_{.90})$  ranges and, for PCBs and Hg, also from confidence intervals (CIs, P = 95%) – the average levels ( $X_{MEDIAN}$   $X_{MEAN}$ ) measured in the



**Fig. 3** | *Cadmium (Cd), mercury (Hg), and lead (Pb) concentration distributions in clams and mussels from the Venice lagoon northern and southern (left boxes) and central (right boxes) districts, according to the data summarized in Tables 1 and 2. To deal with normal distributions, the original data – expressed in \mu g g^{-1} fresh weight for the three heavy metals – were converted to their square roots ([x]<sup>0.5</sup>) for Cd and Pb and natural logarithms (ln[x]) for Hg, as shown in the figure.* 

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**Table 3** | Statistical layout of the selected persistent organohalogenated microcontaminants measured in Venice lagoon clams and mussels.<sup>a</sup> All data reported on a fresh weight base and rounded off to a maximum of three figures

| Statistical descriptors <sup>b</sup>  | Southern<br>and northern<br>districts                                    | Central district  |  |  |  |
|---|--|---|--|--|--|
| Polychlorobiphenyls (ng g-1)  |  |   |  |  |  |
| N<br>$X_{MIN} - X_{MAX}$<br>$X_{MEDIAN}$<br>$X_{MEAN}$<br>CI (95%)<br>$Q_{\bullet 10} - Q_{\bullet 90}$                                 | 28<br>0.650 - 20.7<br>6.74<br>6.64<br>4.83 - 9.13<br>2.46 - 17.3         | 23<br>1.41 - 87.9<br>4.80<br>6.65<br>3.93 - 11.2<br>1.49 - 60.2       |  |  |  |
| Polychlorinated dibenzodioxins and dibenzofurans (pgTE g $^{\text{-1}})^{\circ}$  |  |   |  |  |  |
| N<br>X <sub>MIN</sub> - X <sub>MAX</sub><br>X <sub>MEDIAN</sub><br>X <sub>MEAN</sub><br>CI (95%)<br>Q <sub>•10</sub> - Q <sub>•90</sub> | 40<br>0.064 - 1.46<br>0.312<br>0.273<br>0.219 - 0.339<br>0.087 - 0.571   | 24<br>0.196 - 5.45<br>0.639<br>0.729<br>0.542 - 0.979<br>0.363 - 1.79 |  |  |  |
| Polychlorinated dibenz  | odioxins and dibenzof  | urans (pgTE g <sup>-1</sup> ) <sup>d</sup>                            |  |  |  |
| N<br>X <sub>MIN</sub> - X <sub>MAX</sub><br>X <sub>MEDIAN</sub><br>X <sub>MEAN</sub><br>CI (95%)<br>Q <sub>•10</sub> - Q <sub>•90</sub> | 40<br>0.065 - 1.30<br>0.303<br>0.259<br>0.208 - 0.323<br>0.085 - 0.567   | 32<br>0.166 - 5.31<br>0.779<br>0.799<br>0.619 - 1.03<br>0.380 - 1.89  |  |  |  |
| Hexachlorobenzene (ng g <sup>-1</sup> )   |  |   |  |  |  |
| N<br>X <sub>MIN</sub> - X <sub>MAX</sub><br>X <sub>MEDIAN</sub><br>X <sub>MEAN</sub><br>CI (95%)<br>Q <sub>•10</sub> - Q <sub>•90</sub> | 27<br><0.005 - 0.830<br>0.120<br>0.096<br>0.056 - 0.164<br>0.019 - 0.560 | 20<br>0.084 - 18.0<br>1.58<br>1.71<br>0.874 - 3.36<br>0.372 - 12.6    |  |  |  |
| (a) Estimatos obtainad fuom   | log normal tugue forme at  |   |  |  |  |

<sup>(a)</sup>Estimates obtained from log-normal transformation.

<sup>(b)</sup>CI, confidence interval; Q, percentile.

<sup>(c)</sup>WHO-TEQs.

 $^{(d)}I$ -TEQs.

central district biota are in general 2 - 3 times higher than the corresponding descriptors of the biota from the other two districts. The greatest deviations from the aforesaid pattern are observed for PCBs, HCB, and Hg: HCB exhibits average concentrations in the central district much larger (some 18 times) than elsewhere in the lagoon, whereas the average concentration values of the other two contaminants seem to be rather even.

The calculated *t* values for the differences between the means of congruent distributions are well above the null (H<sub>0</sub>) hypothesis rejection threshold  $t^*$  for – in decreasing order of the  $(t - t^*)$  magnitude – HCB,

PCDDs+PCDFs, Pb, and Cd. In particular, the estimated values of t (and their P) vs their tabulated critical values at P = 0.05 for HCB, PCDDs+PCDFs (WHOand I-TEQs), Pb, and Cd are: 7.0 (P < 0.001) and 2.9\*; 5.5 and 6.8 (P < 0.001) and 2.9\*; 4.6 (P < 0.001) and  $3.0^*$ ; 4.0 (P < 0.001) and 2.0\*. No significant differences were detected for PCB and Hg data distributions based on the t values. By associating results of chemicals which showed a significant difference of the two distributions to sampling sites, the rejection of the null (H<sub>a</sub>) hypothesis also indicates the existence of a significant difference between sampling site contamination levels. Based on Student's t-test outcomes and their level of confidence P, of all the chemicals considered HCB and PCDDs+PCDFs appear to have a higher discriminatory power.

By evaluating the statistical outcome summarized in *Table 3* and *Table 4* against the applicable MLs of the European regulations, the following conclusions may be drawn: the average estimates ( $X_{MEDAN}$  and  $X_{MEAN}$ ) of the chemical distributions considered are well below the pertinent ML values of, respectively, HCB,

**Table 4** | Statistical layout of the selected heavy metals measured in Venice lagoon clams and mussels. All data reported on a fresh weight base and rounded off to a maximum of three figures

| Statistical descriptors <sup>a</sup>  | Southern and northern districts  | Central district  |
|---|--|---|
| Cadmium (µg g <sup>-1</sup> ) <sup>b</sup>  |  |   |
| N<br>X <sub>MIN</sub> - X <sub>MAX</sub><br>X <sub>MEDIAN</sub><br>X <sub>MEAN</sub><br>CI (95%)<br>Q <sub>•10</sub> - Q <sub>•90</sub> | 28<br>≈0.002 - 0.599<br>0.137<br>0.123<br>0.082 - 0.173<br>0.026 - 0.345 | 20<br>0.141 - 1.35<br>0.282<br>0.362<br>0.257 - 0.486<br>0.154 - 0.939    |
| Mercury (µg g-1) °  |  |   |
| N<br>X <sub>MIN</sub> - X <sub>MAX</sub><br>X <sub>MEDIAN</sub><br>X <sub>MEAN</sub><br>CI (95%)<br>Q <sub>•10</sub> - Q <sub>•90</sub> | 28<br>≈0.004 - 0.480<br>0.043<br>0.051<br>0.034 - 0.076<br>0.015 - 0.259 | 20<br>≈0.006 - 0.150<br>0.054<br>0.047<br>0.031 - 0.071<br>≈0.009 - 0.139 |
| Lead (µg g <sup>-1</sup> ) <sup>b</sup>   |  |   |
| N<br>X <sub>MIN</sub> - X <sub>MAX</sub><br>X <sub>MEDIAN</sub><br>X <sub>MEAN</sub><br>CI (95%)<br>Q <sub>*10</sub> - Q <sub>*90</sub> | 16<br>0.010 - 0.420<br>0.161<br>0.159<br>0.110 - 0.217<br>0.023 - 0.289  | 17<br>0.063 - 1.09<br>0.430<br>0.429<br>0.312 - 0.565<br>0.192 - 0.843    |

<sup>(a)</sup> CI, confidence interval; Q, percentile.

<sup>(b)</sup> Estimates from an intermediate normally distributed set of values obtained from the square-root transformation of original data.

<sup>(c)</sup> Estimates obtained from log-normal transformation.

PCDDs+PCDFs, Pb, and Cd [12, 13]. However, small although variable fractions of the central district biota appear to exceed one or more of the aforesaid MLs whereas the probability that biota of the southern and northern districts exceed the acceptance levels is in general negligible. These findings and the contaminant distribution patterns indicate that contamination levels by-and-large comply with food safety conditions, but the central district may require specific management strategies aimed at identifying those areas where the probability to find contaminant levels exceeding the pertinent regulations is higher. In particular, the highest concentrations of PCDDs+PCDFs and Cd in the central district exceed the European MLs, whereas the corresponding value for Pb is borderline with the pertinent ML [12, 13]. Furthermore, in the central district for high end exposure population groups the combined exposure to more than one toxic chemical should be taken into account.

Therefore, biota contamination levels seem to reflect local environmental contamination levels in a clear and unambiguous way, an issue also described elsewhere [22]. Alternative hypotheses such as the presence of a diffused contamination due to many different point sources were not consistent for the chemicals indicated that, in particular, may be correlated to industrial activities insisting on the central district. The analysis presented here seems to have a

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potential to be utilized in the decision-making process concerning future management actions. For example, a recent strategy locally developed in a specific decision-analysis process included the transport of small size clams (under the commercial size) collected in the lagoon central district, forbidden to fishing, to background areas situated in the southern district [23] for the clearance of chemicals of concern before being marketed. Clearance times were selected on the basis of field studies [15] showing that a minimum of a few months were necessary to reach background levels. Therefore, the quantitative and qualitative influence of Porto Marghera and Venice on chemical levels in the lagoon biota is an issue relevant to every management strategy, whose target be the safe consumption of the organisms of interest and the protection of the market.

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