

## POPs IN THE LAGOON OF VENICE: BUDGETS AND PATHWAYS

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### Abstract

Dioxins and furans (PCDD/Fs), polychlorobiphenyls (PCBs) and hexachlorobenzene (HCB) in the ecosystem of the Lagoon of Venice were studied, in order to provide a general picture of conditions in the Lagoon in terms of contamination by persistent organic pollutants (POPs). We present here novel data on atmospheric deposition, water, sediment and clam samples collected in the Lagoon during the period January 2001-December 2004. Atmospheric deposition was sampled monthly at six sites located both close and far from large industrial and urban sources. Water samples were collected monthly from fifteen stations, and twenty-five samples of sediments and clams (*Tapes philippinarum*) were collected in four areas where clams are farmed and harvested inside the Lagoon. All samples

were analysed for PCDD/Fs, PCBs and HCB by HRGC/HRMS in the same laboratory. All samples examined (atmospheric deposition and water) substantially confirmed the spatial pattern reported in previously published data on sediments and atmospheric deposition: the zone surrounding the Porto Marghera petrochemical plant always had the highest levels of POPs (i.e., PCDD/Fs: atmosphere  $\sim 6$  pg of 2,3,7,8-TCDD equivalents (I-TE)  $\text{m}^{-2}\text{d}^{-1}$ ; water  $0.37$  pg I-TE  $\text{l}^{-1}$ ; sediment:  $300$  ng  $\text{kg}^{-1}$ ; clam  $2.8$  pg I-TE  $\text{g}^{-1}$ ), and the minima were found at points on the margins of the Lagoon (PCDD/Fs: atmosphere  $\sim 1$  pg I-TE  $\text{m}^{-2}\text{d}^{-1}$ ; water  $0.05$  pg I-TE  $\text{l}^{-1}$ ; sediment:  $\sim 5$  ng  $\text{kg}^{-1}$ ; clam  $\sim 0.2$  pg I-TE  $\text{g}^{-1}$ ). Intermediate values were often encountered in the historical city centre of Venice and in the central part of the Lagoon. To confirm this, new data on correlation between levels of PCDD/F in sediments and clams are reported, both for absolute values and for the PCDD/F “fingerprint”. There is always a clear fingerprinting signature ( $\text{PCDF}/\text{PCDD} > 1$ ) for samples collected near Porto Marghera, and the opposite ( $\text{PCDF}/\text{PCDD} < 1$ ) in the rest of the Lagoon.

*Keywords:* Atmospheric deposition; Water concentration; Sediment and clam concentrations; Dioxins and furans; Polychlorobiphenyls; Hexachlorobenzene.

## **1. Introduction**

The rapid deterioration of the world’s major ecosystems has intensified the need for effective monitoring and development of operational indicators of ecosystem health

(Costanza and Mageua, 1999), and the extension of health hazard to describe regional ecosystems is a response to accumulating evidence that human-dominated ecosystems have become highly dysfunctional. The Lagoon of Venice is probably one of the world's best-known examples of an ecosystem that has historically been influenced by human intervention since the 15th century. The area has a long history of industrial activity, which peaked after World War II with the construction of oil refineries and several chemical production plants around the Lagoon. Only recently have the environmental problems of Venice been recognised, mainly due to POPs accumulating in sediments and seafood (Marcomini et al., 1997; Jimenez et al., 1998; Green et al., 1999a; Green et al., 1999b; Alcock et al., 2002) – a fact which has aroused concern.

The problem of water pollution in the Lagoon of Venice is very complex, due to the many sources of pollution and the unusual nature of the environment. The Lagoon receives wastewater and several pollutants from a whole series of industries and towns, which include: i) the cities of Venice and Chioggia, with their considerable influxes of tourists, and beaches, coastal strips and islands which, for the main part, lack a proper sewage network and water treatment facilities; ii) the Venetian mainland, which again has an incomplete sewage network and only a few treatment facilities in operation; iii) the two industrial zones and the power station of Porto Marghera; iv) the towns of the Venetian district, which discharge their wastewater into watercourses draining into the Lagoon; v) a surface area of approximately 185,000 hectares, where agriculture is practised using organic and inorganic fertilisers, pesticides, etc., which eventually drain into the Lagoon by way of natural watercourses and channels for the reclamation zones; vi) the passage of shipping, which discharges into the Lagoon waste deriving from incomplete fuel combustion, including

leakage of hydrocarbons; vii) road traffic in neighbouring areas, which presumably also affects the Lagoon.

The massive pollutant load deriving from all these sources exceeds the capacity of the Lagoon successfully to regenerate water, re-mineralise organic compounds, and dilute inorganic ones, so that the concentrations of the various substances can return to levels comparable with those in sea water (Ghetti and Passino, 1980; COMUNE DI VENEZIA - WWF, 1985; MAV - CVN, 1999; MAV-CVN, 2000). A recently published book (Guerzoni and Raccanelli, 2004), containing contributions from several scientists, summarised available data on industrial wastes, foodstuffs, and the possible biologically disrupting effects of POPs in the Lagoon of Venice. It is well-known that one important effect of ecosystem degradation is increased risk to the health of human populations. In the case of POPs, the simplest way for humans to be exposed is through the consumption of food contaminated by dioxins and PCBs. Due to long-term exposure to these pollutants and bio-accumulation, even minimal doses of dioxins and PCBs can result in negative effects on health (Czub and McLachlan, 2004).

This paper gathers together novel data, with a review of recently published data on dioxins, PCBs and HCB, related both to the environment and to human health, in order to emphasise the need for intervention.

These new data consider atmospheric deposition and water samples from the entire Lagoon and sediments and clams from a few fishing areas. Sediment data reported here (dots in Fig. 2) derive from various papers (Marcomini et al., 1997; Marcomini et al., 1999; MAV-CVN, 2000; Bellucci et al., 2000; Wenning et al., 2000; Frignani et al., 2001; Bernstein et al., 2002; Raccanelli et al., 2004).



## **2. Materials and Methods**

### Atmospheric deposition sampling

Forty-two new atmospheric deposition samples were collected monthly (i.e., every  $29\pm 6$  days) at six sites (triangles in Fig. 1) in the period February-December 2004, thus integrating previous sampling lasting one year (March 2003-February 2004). The sampling sites were located respectively: in the city of Venice, upwind from the atmospheric emissions from the main industrial district (IBM); inside and about 5 km downwind (south west) of the industrial zone of Porto Marghera (EZI and DOG, respectively); in the central lagoon, in two sites far from large industrial and urban sources (L2, L3), and in one site near the industrial zone (L1).

Atmospheric depositions were collected by 6 bulk samplers, already described in previous papers (Guerzoni et al., 2004; Rossini et al., 2005). The samplers were polymer structures, formed of a cylindrical container and a protection ring to avoid damage caused by birds and animals, clamped to a pole more than 1.5 m high. Organic micropollutants were collected in a Pyrex bottle with a Pyrex funnel, previously silanized with dimethyldichlorosilane 5 % in toluene, to prevent retention of analytes. Operations for cleaning and silanisation are described in details in Raccanelli et al. (2002) and Guerzoni et al. (2004).

### Water sampling

A total of two hundred water samples were collected monthly by the Water Authority during 2001-2002, from fifteen stations in the Lagoon (squares in Fig. 1). Most of the sampling points were located close to sources of urban and industrial pollution, in order to quantify the direct influence of substances discharged into the Lagoon. For purposes of

comparison, three points, relatively distant from the points of discharge, were included, with the aim of checking the extent of variations in parameters with respect to the points closest to the sources.

Samples of POPs were collected with an automatic system capable of concentrating organic micro-pollutants in a solid phase. This system (INFILTREX 100-II, Axys Environmental System) collects all POPs, both adsorbed on suspended particulate matter (SPM) and dissolved in large volumes of water (up to 35 litres) on a glass wool filter and XAD2 resin cartridges. In terms of total concentrations of POPs in water (sum of the fraction dissolved and adsorbed on SPM), the extraction, elution and successive analysis of samples resulted in measurements with a sensitivity one hundred times higher than that of traditional methods of analysis.

#### Sampling of sediments and clams

Samples of sediments and clams (*Tapes philippinarum*) were collected concurrently during this study in the north, central and south Lagoon, in areas where clams are farmed and harvested, and in the industrial zone, where all types of fishing and harvesting are forbidden but where unauthorised activities do take place (circles in Fig. 1). Each sediment sample reflects the composition of ten subsamples of superficial sediments (10 cm), separately collected and then homogenised. Sampled clams were only specimens larger than the authorised market size, which is 25 mm and is usually reached at the age of 18 months. Concentrations of PCDD/Fs, PCBs and HCB in all sediment samples were calculated on a dry weight basis. The moisture content of each sediment sample was determined by drying a

separate sub-sample of sediment overnight in a conventional oven at 105 °C. Concentrations in clam flesh are expressed on a wet weight basis.

Sediment samples were transported on ice and stored at 4°C. They were thoroughly mixed with a stainless steel spatula, in order to obtain 10.0±0.1 g subsamples. Clam flesh was rinsed with distilled water, homogenised, freeze-dried and ground, and 10.0±0.1 g subsamples were transferred to glass beakers.

#### Determination of POPs

The following organic compounds were analysed by HRGC/HRMS in samples of atmospheric bulk deposition, water, sediments and clams: polychlorobiphenyls (PCBs), hexachlorobenzene (HCB) and polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs). All solvents (n-hexane, dichloromethane, acetone, toluene, ethylacetate) were Picograde<sup>®</sup> reagent grade (Pomochem GmbH, Wesel, Germany). Native and <sup>13</sup>C<sub>12</sub>-labelled PCDD/Fs, PCB and HCB standards were purchased from Cambridge Isotope Laboratories (Woburn, MA, USA). Samples were first spiked with a series of 15 <sup>13</sup>C<sub>12</sub>-labelled 2,3,7,8 PCDD/Fs, 12 <sup>13</sup>C<sub>12</sub>-labelled PCB, and <sup>13</sup>C<sub>12</sub>-HCB substituted isomers as internal standards, and then extracted. Water and atmospheric bulk deposition samples were extracted in a separatory funnel with dichloromethane (4x50 mL). Sediment and clam samples were extracted by ASE 200 (DIONEX Sunnyvale, CA) in 50 mL of toluene at 135 °C, 2000 psi, 7 min heat-up and 2 cycles of 10 min static time. Extracts were transferred to hexane before clean-up treatment. The extracts were first spiked with <sup>37</sup>Cl<sub>4</sub>-labelled 2,3,7,8 PCDD and 3 <sup>13</sup>C<sub>12</sub>-labeled PCB, and then cleaned with sulphuric acid (98%) and potassium hydroxide (20%) in a 100-mL separatory funnel. Clean-up was performed by an automatic system

(Power Prep. Fluid Management System, Inc.) with 3 pre-packed disposable columns containing multilayer silica, alumina and carbon.. Extracts were treated and then cleaned using the automatic three-column system with pre-packed disposable columns containing multilayer silica, alumina and carbon for.

PCDD/Fs, PCB and HCB HRGC/HRMS analyses were carried out on an HP 6890 Plus gas chromatograph coupled to a Micromass Autospec Ultima mass spectrometer, operating in SIR-EI mode at 35 eV and with a resolution of 10,000 (5% valley). PCDD/F, PCB and HCB sample injections were performed in the splitless mode on a 60-m DB5 ms column (J&W 0.25 mm ID, 0.25 µm film) and, for PCDD/Fs only, on a 60-m Rtx 200 (Restek 0.25 mm ID, 0.25 µm film) for verification. Quantitative determination was performed by isotope dilution methods, using relative response factors previously obtained from five standard solution injections (US EPA Method 1613B/94; US EPA Method 1668A/99, POP003 rev.2).

Our laboratory follows UNI CEI EN ISO/IEC 17025 norms, and is accredited for all the analysed parameters. Recoveries always ranged between 50 % and 110 %. Reproducibility was 15 % or better for lower values. Laboratory blanks, repeated twice a week, were lower than 9 % with respect to the minimum concentration found. Overall uncertainty (cover factor  $K=2.45$ ) in analysis of PCDD/Fs and PCBs, calculated at detection limit, was less than 20% for each cogener.

### **3. Results and Discussion**

#### REVIEW DATA

##### Sediments

Several recent reviews have highlighted increasing knowledge of the fact that the Lagoon of Venice was polluted by high levels of dioxin and PCBs after World War II. In particular, in the last 10 years, after claims of sediment pollution (Greenpeace, 1995), new studies of both environmental and human risks have been published.

Several studies used radiometric techniques to define the chronology of sediment contamination. Human activities, canal dredging, the transit of ships and smaller craft which disturbed even deep sediments, and the fishing and harvesting of molluscs carried out with special turbo-blowers have left very few zones undisturbed. Thus, it is difficult if not impossible to carry out a chronological study of lagoon sediments in areas characterised by large-scale human activity. The decision was therefore made to monitor POPs in surface sediments, in order to define their distribution in space, and to measure contamination levels in the habitat of living organisms, which is the compartment responsible for transferring POPs to man. Most of the recent data indicate that, during the period 1950-2000, some 6 kg of I-TE have been emitted, mainly as a by-product of vinyl chloride monomer production. Budget estimates have found most of it (~4 kg) stored inside industrial channels, and more than 1 kg in lagoon sediments (Marcomini et al., 1999).

The first complete study of the presence of POPs in surface sediments (first 15 cm) in the Lagoon of Venice was carried out in 1997 and 1998 by the Consorzio Venezia Nuova on behalf of the Water Authority (MAV-CVN, 2000). Several other studies have been carried out in the same area, so that the sediment data reviewed in this study derive from various

papers (Marcomini et al., 1997; Marcomini et al., 1999; MAV-CVN, 2000; Bellucci et al., 2000; Wenning et al., 2000; Frignani et al., 2001; Bernstein et al., 2002).

For the sake of clarity, we divided the entire Lagoon in three subzones: (i) industrial zone; (ii) inner lagoon; (iii) outer lagoon (Fig. 1). Average POP data of each of the three subzones are listed in Table 1. The same table also lists the values of sediments collected in the canals of the city of Venice itself (Zonta et al., 2005), together with natural (background) values calculated from dated cores collected inside the Lagoon (Marcomini et al., 1997; Bernstein et al., 2002; Frignani et al., 2001).

Table 1 clearly shows that the industrial channels have maxima for all POPs, with values up to 3 orders of magnitude higher than background values. Data for the inner lagoon areas also show values 20-30 times higher than pre-industrial POP levels. The data for city canal sediments are comparable with industrial ones for PCBs and with the inner lagoon for PCDD/Fs.

Using the background values, we calculated an Integrated Enrichment Factor (IEF) as follows:

$$IEF = [EF_i + EF_j + EF_k] / 3$$

where  $EF_{i,j,k} = C_{i,j,k} / Bk_{i,j,k}$ ,

with  $C_{i,j,k}$  = surface sediment concentration,  $Bk_{i,j,k}$  = background value, and  $i$  = PCBs,  $j$  = I-TE and  $k$  = HCB.

The map of enrichment values in sediments (Fig. 2) highlights areas which may be considered “hot spots” ( $IEF > 20$ ), due to enriched contents of POPs, like most of the area off the industrial zone of Porto Marghera, with median IEF values of 112 and some IEF values inside the industrial channels up to 800 (Table 2). Most of the outer lagoon sediments

showed IEF values  $< 5$  (mean 3), relatively close to background levels, whereas the inner (west) part of the Lagoon has largely intermediate values ( $5 < \text{IEF} < 20$ ). The average IEF value of 9 is an evident signal of sediment contamination, one order of magnitude higher than the background POP levels. In this class, the contribution of PCBs to IEF prevails, whereas HCB makes the main contribution to IEF in the other two classes ( $< 5$  and  $> 20$ ).

## NEW DATA

### Atmospheric deposition fluxes

In previous works (e.g., Rossini et al., 2001; Guerzoni et al., 2004; Rossini et al., 2005), it was shown that differences in the mean bulk deposition fluxes of POPs among sampling stations inside the Lagoon were clearcut and that atmospheric depositions at industrial sites were higher than target values for dioxin deposition as recommended by the EU strategy on dioxins, furans and polychlorobiphenyls. The new data, listed in Table 3, confirm those findings by adding almost one year of data. Differences between the industrial zone, urban and outer lagoon sites are evident; in particular, only a few kilometres (2-5) from the principal sources of emissions (located inside the industrial zone), there is a significant drop in PCDD/F and HCB deposition fluxes, from  $\sim 200$  to  $\sim 50 \text{ pg m}^{-2} \text{ d}^{-1}$  and from  $\sim 3000$  to  $\sim 100 \text{ pg m}^{-2} \text{ d}^{-1}$ , respectively. The same pattern is evident for deposition values in terms of toxicity, with three times higher average values in the industrial zone ( $\sim 6 \text{ pg I-TE m}^{-2} \text{ d}^{-1}$ ) as compared with the rest of the Lagoon ( $< 2 \text{ pg I-TE m}^{-2} \text{ d}^{-1}$ ). This trend is slightly different for PCBs, with peaks in the industrial zone ( $\sim 9000 \text{ pg m}^{-2} \text{ d}^{-1}$ ) but still significant deposition values in the inner lagoon ( $\sim 2500 \text{ pg m}^{-2} \text{ d}^{-1}$ ), which indicate other sources than industry in the city of Venice (boat traffic, urban activities, glass-works, etc.). In conclusion, the main

feature is that fluxes from the atmosphere of all POPs were two to ten times higher in stations in the industrial zone than in the other areas, also affecting POP deposition in the inner lagoon.

As already reported in a previous paper (Guerzoni et al., 2004), comparisons of patterns of PCDD/F homologue groups in atmospheric deposition samples collected inside the Lagoon show significant differences, with a clear fingerprinting signature (PCDF > PCDD) in most of the samples collected near the industrial zone. In particular, three different patterns were found: far from the industrial zone, 8CDD and 7CDD made the prevailing contributions to  $\Sigma$ PCDD/F loading; in the other two profiles (both characteristic of industrial fall-out), OCDF made a different contribution to  $\Sigma$ PCDD/F loading, increasing from ~20% to ~40% and reaching values of >70%, thus reversing the PCDD/PCDF ratio from <1 to  $\cong$ 2.

#### Water concentrations

Water samples collected in fifteen stations in the Lagoon showed a very high variability among sites (Table 4). Mean dioxin and HCB values were much higher in the channels of the industrial zone (PCDD/F = 15  $\text{pg l}^{-1}$ ; HCB = 280  $\text{pg l}^{-1}$ ), compared with the rest of the Lagoon (PCDD/F = 2  $\text{pg l}^{-1}$ ; HCB = 28  $\text{pg l}^{-1}$ ). Instead, comparable PCB values (~160  $\text{pg l}^{-1}$ ) were found in both industrial channels and city canals, and were three times higher than the general Lagoon data (~50  $\text{pg l}^{-1}$ ). Toxicity values (PCDD/Fs) of the whole Lagoon were in the range 0.05-0.20 (mean 0.10)  $\text{pg I-TE l}^{-1}$  - much higher than the threshold limit value established by the Italian Ministry of the Environment of 0.013  $\text{pgTE l}^{-1}$  (MAV, 2002). In the industrial zone, PCDD/Fs peaked to 0.40- 0.50  $\text{pg I-TE l}^{-1}$ .

The differences between the overall values of PCDD/Fs at various points is shown in Fig. 3, giving three examples of the relative abundances of homologue groups (fingerprints). The highest values were measured at Porto Marghera (points D, F) and in the Grand Canal (point A) - both areas where concentrations of these compounds also peak in sediments. At points further away from the generating sources, concentrations are lower or even absent (points L, N, Q, R).

Comparison of the relative abundances of homologues reveals several differences between the fingerprints at the various points. Those close to the Porto Marghera industrial zone (points d, e, f) highlight the specific superiority of OCDF (50-60%, compared with all homologue groups), as well as 1,2,3,4,6,7,8 HpCDF and OCDD (10-20%). This picture is comparable with that reported in the literature concerning discharges and waste from the production of dichloroethylene (DCE) and vinyl chloride (VCM), and confirms that the characteristics of the water in the industrial zone has the PCDD/PCDF fingerprint typical of chlorinated hydrocarbons (DCE/VCMs), which continue to be produced in the petrochemical plant (Fig. 3, station D). A second group of points (i, p, l) is characterised by the clearcut dominance of OCDD over the other homologues. These points are the furthest from the industrial zone and consequently may not be affected by fluxes from that area. The dioxin fingerprint at these points is typical of the general processes of combustion and contamination due to urban discharges (Fig. station I). A third group of points (a, b, c, g, h, m, o) has OCDD and OCDF in comparable concentrations. These points are clearly influenced by a combination of the two main sources: Porto Marghera for OCDFs and the widespread urban contribution for OCDDs (Fig 3, station B).

These observations confirm the need for intervention with rigorous anti-pollution measures, both as regards discharges directly into the Lagoon and throughout the drainage basin, and interventions aiming at reducing sources of pollution everywhere (e.g., dredging of contaminated sediments, work on the margins of the Porto Marghera zone to eliminate leakages from contaminated industrial soil).

#### Sediment and clam concentrations

Samples of sediments and clams (*Tapes philippinarum*) were collected concurrently during 2003 in three areas where clams are farmed and harvested, and also in the industrial zone, where all types of fishing and harvesting are forbidden but where unauthorised activities do take place (circles in Figs. 1 and 2). The clam samples used were only specimens larger than the market size, which is 25 mm and is usually reached in 18 months. The contamination levels of the sediments in the three fishing areas were quite similar, with a slightly higher level in the north, and much higher values in the industrial zone, as also evidenced by IEFs (see Fig. 2). The same also applies to POP levels in clam flesh, with quite similar toxicity values in the three areas of  $\sim 0.1\text{-}0.2$  (range 0.06-0.27) pgWHO-TE g<sup>-1</sup> (PCDD/F + PCB, Van den Berg et al., 1998) - almost one order of magnitude lower than those of  $\sim 1.8$  (range 1.2-2.8) pgWHO-TE g<sup>-1</sup> found in industrial channels where fishing is forbidden.

Concentrations of dioxin and “dioxin-like” PCBs in clam flesh from the Lagoon may be correlated with those found in sediments. As Fig. 4 shows, the regression between the logarithms of the I-TE in clam flesh and sediments was statistically significant. The log-log

regression explains more than 70% of the variance of equivalent toxicity, thus providing further proof that contamination of clams is related to contamination in sediments. The relative abundances of the homologue groups, in both sediments and clams (fingerprints) are shown in Fig. 5.

Visual inspection of the fingerprints strongly suggests that the sources of contamination in the three monitored areas are different. In particular, the fingerprint for both sediments and the clams near the industrial zone (Fig. 5 A) was characterised by the highest percentage of OCDF, about 70% in sediments. This substance was and still is released into the environment as a result of the chlorine, PVC and chlorinated hydrocarbon production. The percentage of OCDF was lower in the other three areas and lowest in the southern Lagoon (Fig. 5 D), where the fingerprint was characterised by the highest percentage of OCDD. This compound is usually found in the discharges of urban wastewater treatment plants, and may also be released into the environment by combustion processes and ships' engines. The other two fingerprints presented here contained similar percentages of the above congeners, indicating that the central and north lagoon (Fig. 5 B,C) are affected by both urban wastewater and industrial pollution. However, the fact that the percentages for OCDF are higher than those of OCDD suggest that, in both areas, contamination is related directly or indirectly to industrial activities. It is also interesting to note that the fingerprints in clams and sediments from the same area are remarkably similar, and characterised by concentrations of TCDF higher in clams than in sediments. This finding supports the hypothesis that sediments are still the main source of clam contamination, as also suggested by a quantitative relationship between equivalent toxicities in abiotic and biotic compartments (Fig. 4).

From the viewpoint of the health risk for local regular clam consumers, it should be noted that equivalent toxicities within the three monitored areas are very similar and not very high. In fact, if the average,  $0.153 \text{ pg WHO-TE g}^{-1} \text{ w.w.}$  is multiplied by a daily dose of  $15 \text{ g day}^{-1}$ , daily intake is  $2.3 \text{ pg/day}$ . However, it must be pointed out that the situation is different if we consider that illegal harvesting of *Tapes philippinarum* is still practised in the most contaminated area and that clams are still sold in the local market. In this case, with mean data of  $\sim 2 \text{ pg WHO-TE/g w.w.}$ , consumption of *Tapes philippinarum* represents a threat for the health of a small percentage of local regular consumers.

#### **4. Conclusions**

It is clear from most of the data published until now that the industrial zone of Venice and the lagoon facing it are the parts of the basin which are most highly polluted by POPs. Here, POP values of water and atmospheric deposition fluxes are one to two orders of magnitude higher than background values, and the whole central part of the Lagoon contains more than 5 times pre-industrial levels. POPs show the same trends already highlighted in sediments collected in the Lagoon.

Integrated Enrichment Factors (IEF), calculated as the sum of the ratio of PCB, PCDD/Fs and HCB with pre-industrial (background) values, confirmed that the industrial zone is a “hot spot” for sediment pollution.

As regards contamination pathways, the fact that the fingerprints for sediments and clams sampled in the same areas were very similar indicates that sediments are the main source of contamination.

In addition to influencing the quality of water at these points through wastewater discharge, contaminated areas and sediments from the industrial zone, the industrial component is also detected in atmospheric fall-out of industrial origin, as clearly demonstrated by the present study, using both new and past data.

From the viewpoint of the health risk, it is shown that the consumption of *Tapes philippinarum* from illegal fishing, still practised in the most contaminated area, represents a threat for the health of a small percentage of local regular consumers.

In conclusion, there is a clearcut need for remedial action in the Lagoon of Venice, so that this fragile ecosystem, which has succeeded in cohabiting with man for over a thousand years, can gradually heal the wounds it has suffered thanks to human activity, and can be safeguarded from the further threat of pollution. Monitoring is indispensable, so that the efficacy of remedial measures can be evaluated, and appropriate information about risks for human health and well-being can be made available.

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## References

- Alcock, R.E., Sweetman, A.J., Green, N.J.L., Jones, K.C., Della Sala, S., Canotto, E., Marcomini, A., 2002. PCDD/Fs in venetian foods - a quantitative assessment of dietary intake. In: Pellei, M., Porta, A., Hinchee, R.R. (Eds.). *Characterization of Contaminated Sediments*, Batelle Press, pp. 9-16.
- Bellucci, L. G., Frignani, M., Raccanelli, S., Carraio, C., 2000. Polychlorinated dibenzo-*p*-dioxins and dibenzofurans in surficial sediments of the Venice Lagoon, *Mar. Poll. Bull.* 40, 65-76.
- Bernstein, A.G., Barbanti, A., Ferrari, G., Marcomini, A., Guerzoni, S., Zonta, R., 2002. Sources and occurrence of Persistent Toxic Substances (PTS) in the lagoon of Venice (Italy). UNEPGEF- UNEP Regional Priority Setting Meeting, Barcelona 26-28 June 2002.
- COMUNE DI VENEZIA – WWF, 1995. *Laguna conservazione di un ecosistema*, Arsenale Editrice, Venezia.
- Costanza, R., Mageua, M., 1999. What is a healthy ecosystem?. *Aquatic Ecology* 33, 105-115.
- Critto, A., Marcomini, A., 2001. *Rischio ecologico ed inquinamento chimico lagunare* Libreria Editrice Cafoscarina, Venezia (in Italian).
- Czub, G., McLachlan M.S., 2004. A food chain model to predict the levels of lipophilic organic contaminants in humans. *Environ. Toxicol. Chem.* 23, 2356-2366.
- Frignani, M., Bellocci, L., Carraio, C., Fagotto, M., 2001. Accumulation of Polychlorinated Dibenzo-*p*-Dioxins and Dibenzofurans in Sediments of the Venice Lagoon and the Industrial Area of Porto Marghera. *Mar. Poll. Bull.* 42, 544-553.
- Ghetti, A., Passino, R., 1980. *Ripristino conservazione ed uso dell'ecosistema lagunare veneziano*, Comune di Venezia, Venezia.
- Green, N.J.L., Wood, J., Alcock, R.E., Marcomini, A., Jones K.C. 1999a. PCDD/Fs and PCBs in sediment samples from the Venice lagoon. *Organohal. Comp.* 43, 339-342.
- Green, N.J.L., Wood, J., Alcock, R.E., Della Sala, S., D'Andrea, F., Jones K.C., 1999b. *Organohalogen Compounds* 43, 343.

- Greenpeace, 1995. Morte a Venezia (<http://www.greenpeace.it/archivio/toxic/ven-res.htm>).
- Guerzoni, S., Rossini, P., Molinaroli, E., Ramazzo, G., Raccanelli, S., 2004. Atmospheric deposition of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in the Venice Lagoon, Italy. *Chemosphere* 54, 1309-1317.
- Guerzoni, S., Raccanelli, S., 2004. *The Sick Lagoon*. Libreria Editrice Cafoscarina, Venezia.
- Jimenez, B, Hernandez, L. M., Gonzalez, M.J., Eljarrat, E., Rivera, J., Fossi, M.C., 1998. Congener Specific Analysis of Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans in Crabs and Sediments from the Venice and Orbetello Lagoons, Italy. *Environ. Sc. and Technol.* 32, 3853-3861.
- Marcomini, A., Zanette, M., D'Andrea, F., Della Sala, S., 1997. *Diossine, ambiente e salute*, Arsenale Editrice, Venezia (in Italian).
- Marcomini, A., Della Sala, S., Ferrari, G., Giacometti, A., Guerzoni, S., Raccanelli, S., Zonta, R., 1999. Preliminary budget of dioxins and dioxin-like PCBs in the Lagoon of Venice. *Organohal. Comp.* 41, 481-485.
- MAV (Magistrato alle Acque di Venezia), 2002. *Monitoraggio delle acque della laguna di Venezia. Dati relativi al 2000-2001*. Servizio Antinquinamento del Magistrato alle acque (SAMA), Venice, pp. 91.
- MAV-CVN (Magistrato alle Acque di Venezia - Consorzio Venezia Nuova), 1999. *Interventi per il recupero ambientale e morfologico della laguna di Venezia. Mappatura dell'inquinamento dei fondali lagunari, studi ed indagini. Relazione finale*.
- MAV-CVN (Magistrato alle Acque di Venezia - Consorzio Venezia Nuova), 2000. *Programma generale delle attività di approfondimento del quadro conoscitivo di riferimento per gli interventi ambientali, "Progetto 2023", 6 linee*.
- Raccanelli, S., Guerzoni, S., Rossini, P., Favotto, M., 2002. Monitoring POPs (PCDD/F PCB HCB PAH DDT) in atmospheric deposition: sampling and analytical problems. *Organohalogen Compounds* 58, 49– 52.
- Raccanelli, S., 2004. POPs from sediments to the food chain: the need for monitoring. In: Guerzoni, S., Raccanelli, S. (Eds.). *The Sick Lagoon*. Libreria Editrice Cafoscarina, Venezia, Italy, pp. 47-54.

- Raccanelli, S., Pastres, R., Favotto, M., Vio, P., 2004. Correlation between POPs in sediments and edible bivalve in the Lagoon of Venice and estimation of the daily intake. *Organohalogen Compounds* 66, 1823-1828.
- Rossini, P., De Lazzari, A., Guerzoni, S., Molinaroli, E., Ramazzo, G. Zancanaro, A., 2001. Atmospheric input of organic pollutants to the Venice Lagoon. *Annali di Chimica* 91, 491-501.
- Rossini, P., Guerzoni, S., Matteucci, G., Gattolin, M., Ferrari, G., Raccanelli, S., 2005. Atmospheric fall-out of POPs (PCDD-Fs, PCBs, HCB, PAHs) around the industrial district of Porto Marghera, Italy. *The Science of the Total Environment* 349, 190– 200.
- US EPA Method 1613B/94: Tetra-through octa-chlorinated dioxins and furans by isotope dilution HRGC/HRMS.
- US EPA Method 1668A/99: Chlorinated biphenyl congeners in water soil sediment tissue by HRGC/HRMS.
- Van Den Berg, M., Birnbaum, L.S., Bosveld, B.T.C., Brunstrom, B., Cook, P., Feeley, M., Giesy, J.P., Hanberg, A., Hasegawa, R., Kennedy, S.W., Kubiak, T., Larsen, J.C., Van Leeuwen, F.X.R., Liem, A.K.D., Nolt, C., Petersen, R.E., Poellinger, L., Safe, S., Schrenk, D., Tillit, D., Tysklind, M., Younes, M., Waern, F., Zacharewsky, T., 1998. Toxic equivalency factors (TEFs) for PCBs, PCDDs for humans and wildlife. *Environ. Health Perspect.* 106, 775-779.
- Wenning, R., Dodge, D., Peck, B., Shearer, K., Luksemburg, W., Della Sala, S., Scazzola, R., 2000. Screening-level ecological risk assessment of polychlorinated dibenzo-p-dioxins and dibenzofurans in sediments and aquatic biota from the Venice Lagoon, Italy, *Chemosphere* 40, 1179-1187.
- R. Zonta, L. Zaggia, F. Collavini, F. Costa and M. Scattolin, 2005. Sediment contamination assessment of the Venice canal network (Italy). In: *Flooding and Environmental Challenges for Venice and its Lagoon: State of Knowledge*, Edited by C. A. Fletcher and T. Spencer, Cambridge University Press, 603-616.

Table 1: Average values of PCBs, PCDD/Fs, 2,3,7,8-TCDD equivalents (I-TE) and HCB in sediments of Lagoon of Venice, subdivided by area (see Fig. 1). Background (pre-industrial) values derived from dated cores collected inside Lagoon (Frignani et al., 2001; MAV, 2002) are also shown. City canal data from Zonta et al. (2005).

Zone	PCBs $\mu\text{g kg}^{-1}$	PCDD/F $\mu\text{g kg}^{-1}$	I-TE $\text{ng kg}^{-1}$	HCB $\mu\text{g kg}^{-1}$
Industrial channels	810	14.0	300	260
Inner lagoon	26	1.0	16	2
Outer lagoon	5	0.3	4.0	0.2
City canals	600	0.5	6.0	nd
<i>Background</i>	<i>1</i>	<i>0.03</i>	<i>0.5</i>	<i>0.1</i>

Table 2: Integrated Enrichment Factors (IEFs) of PCBs, 2,3,7,8-TCDD equivalents (I-TE) and HCB in bottom sediments (see text for explanations). Data are plotted in Fig. 2, where an interpolation with two isolines at 5 and 20 IEF are marked. Total number of samples: 102. Data from Marcomini et al. (1999); MAV-CVN (2000); Bernstein et al. (2002).

IEF classes	IEF median	No. of samples	EF <sub>PCB</sub>	EF <sub>I-TE</sub>	EF <sub>HCB</sub>
< 5	3	43	<b>3</b> (1-9)	<b>1</b> (0-6)	<b>5</b> (5-10)
5-20	8	48	<b>10</b> (2-36)	<b>8</b> (0-40)	<b>10</b> (5-30)
>20	112	11	<b>163</b> (11-685)	<b>164</b> (4-921)	<b>529</b> (5-2280)

Table 3: Bulk atmospheric deposition fluxes of PCBs, PCDD/Fs, 2,3,7,8-TCDD equivalents (I-TE) and HCB observed from February to December 2004 in study area. See Fig. 1 for site identification.

Sub-area	Statistics	PCBs pg m <sup>-2</sup> d <sup>-1</sup>	PCDD/Fs pg m <sup>-2</sup> d <sup>-1</sup>	I-TE pg m <sup>-2</sup> d <sup>-1</sup>	HCB pg m <sup>-2</sup> d <sup>-1</sup>
Industrial zone (EZI, DOG)	deposition range	1376-24307	11-975	0-16.8	83- 20249
	mean value	<b>8763</b>	<b>245</b>	<b>5,6</b>	<b>3330</b>
	median value	5646	111	3,5	681
	samples	10	10	10	10
Inner lagoon (L1, L2)	deposition range	183-28921	8-115	0-4.4	4-3031
	mean value	<b>2482</b>	<b>40</b>	<b>1,3</b>	<b>426</b>
	median value	821	25	0,9	144
	samples	18	18	18	18
Outer lagoon (L3)	deposition range	213-1431	9-64	0-2.5	4-272
	mean value	<b>591</b>	<b>26</b>	<b>0,9</b>	<b>110</b>
	median value	568	16	0,5	103
	samples	9	9	9	9
City of Venice (IBM)	deposition range	814-1315	12-146	0-3.4	4-286
	mean value	<b>1109</b>	<b>66</b>	<b>1,5</b>	<b>110</b>
	median value	1082	55	1,7	92
	samples	5	5	5	5

Table 4: Average values of PCBs, PCDD/Fs, 2,3,7,8-TCDD equivalents (I-TE) and HCB in water samples collected in 15 stations of Lagoon of Venice (see Fig. 1 for site locations), and same data subdivided by sub-area.

Site	PCB pg l <sup>-1</sup>	PCDD/F pg l <sup>-1</sup>	PCDD/F pg I-TE l <sup>-1</sup>	HCB pg l <sup>-1</sup>
a	397	12,2	0,26	90
b	57	3,1	0,08	20
c	45	1,7	0,04	70
d	199	28,9	0,46	240
e	208	9,0	0,18	310
f	76	13,3	0,46	290
g	40	2,8	0,05	30
h	88	3,4	0,11	40
i	65	1,5	0,04	20
l	31	0,5	0,00	20
m	9	1,4	0,03	20
o	122	4,0	0,10	20
p	48	1,9	0,05	30
q	4	0,4	nd	10
r	41	0,4	nd	60
Industrial channels	161	17	0,37	280
Lagoon	50	2	0,05	28
City canals	166	6	0,12	60

Figure 1

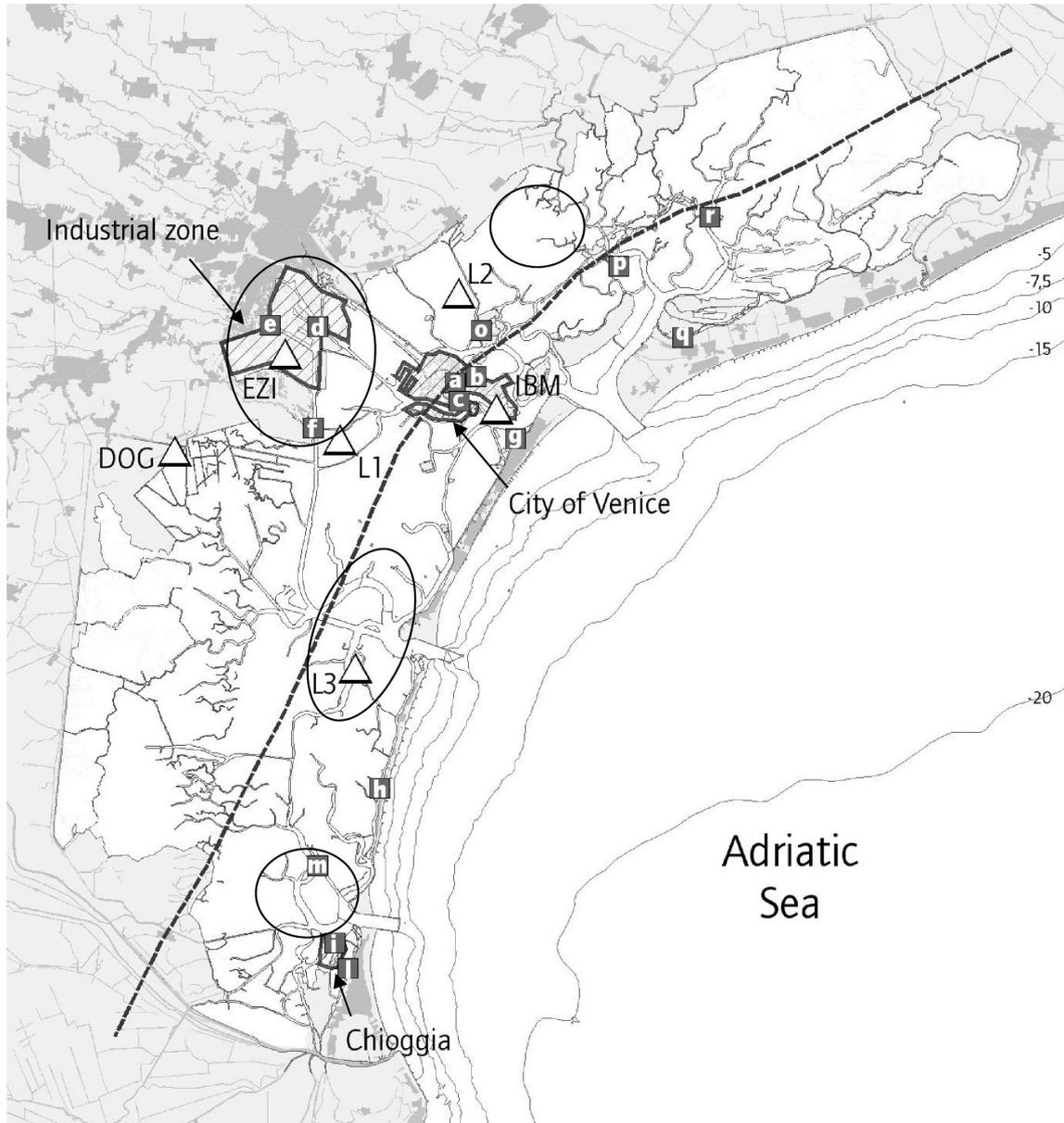


Figure 2

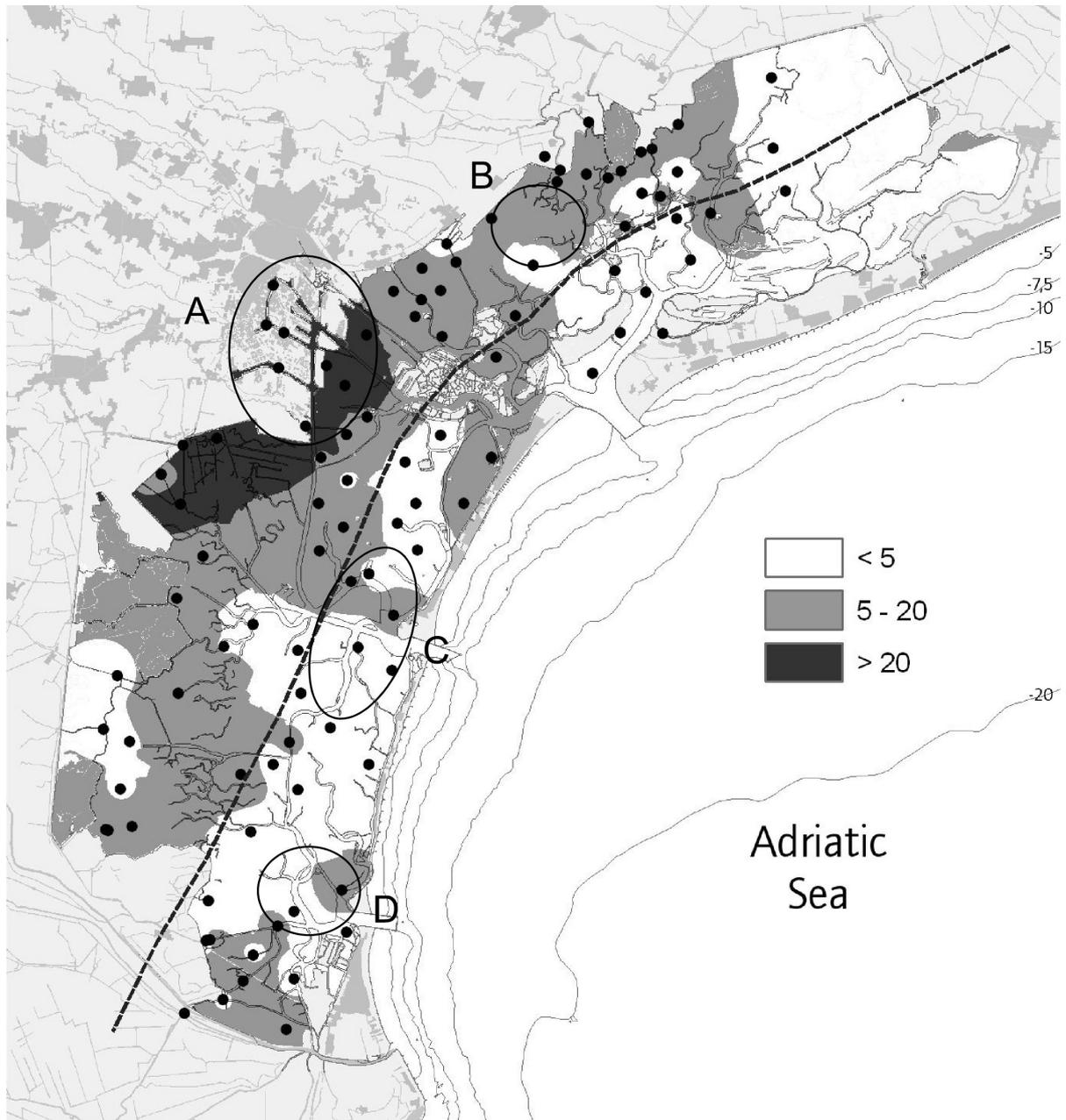


Figure 3

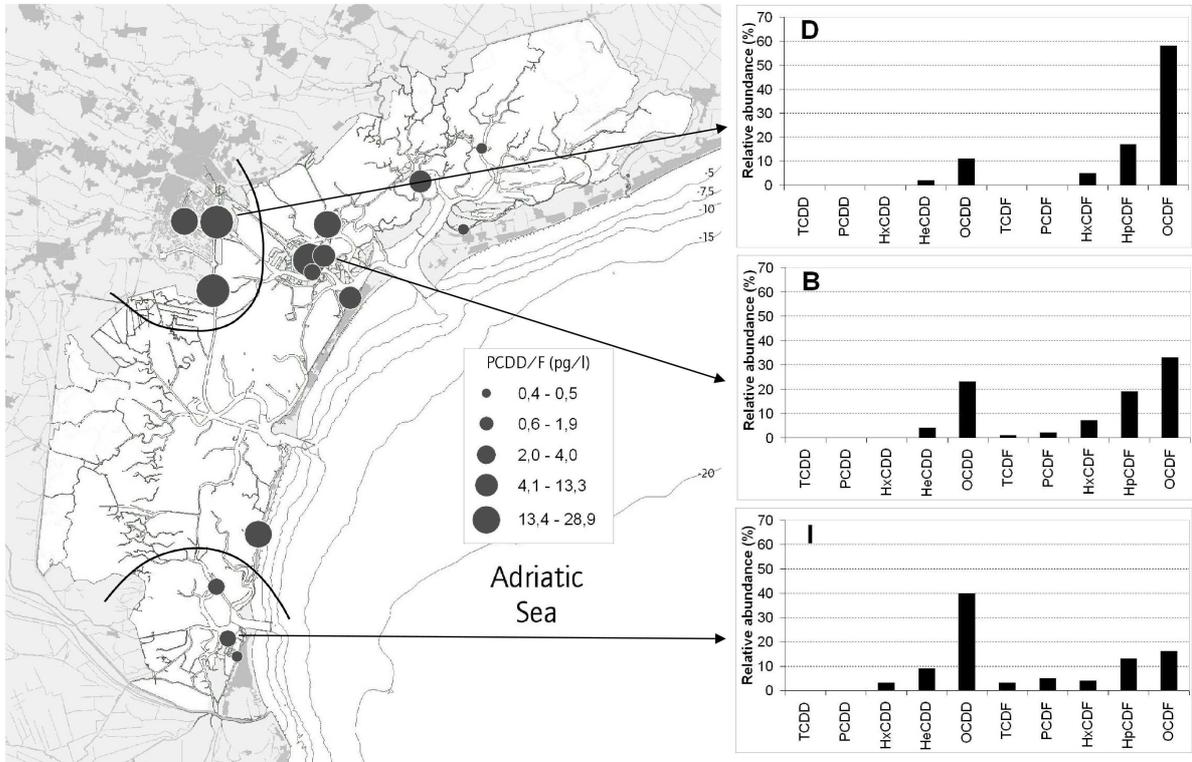


Figure 4

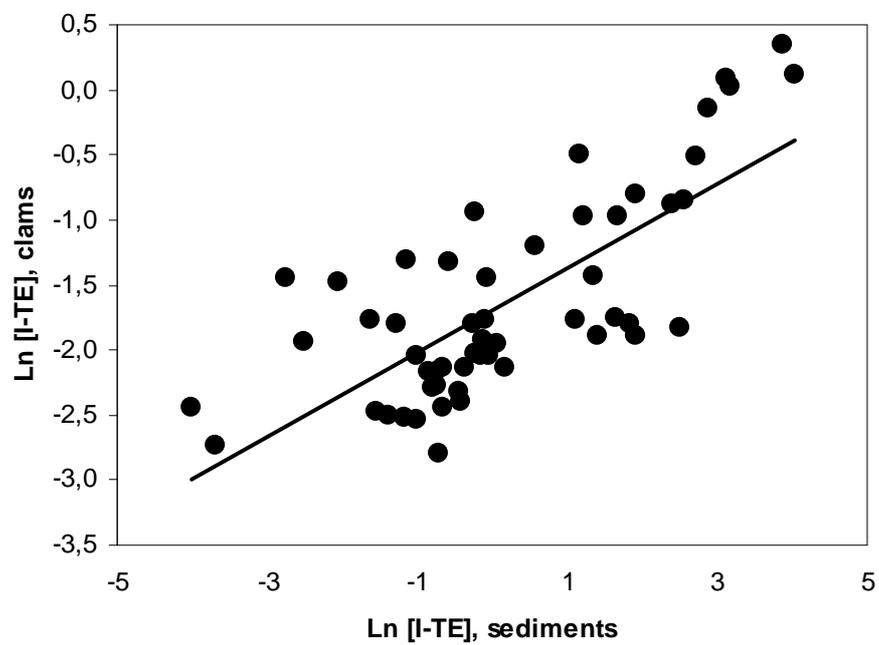
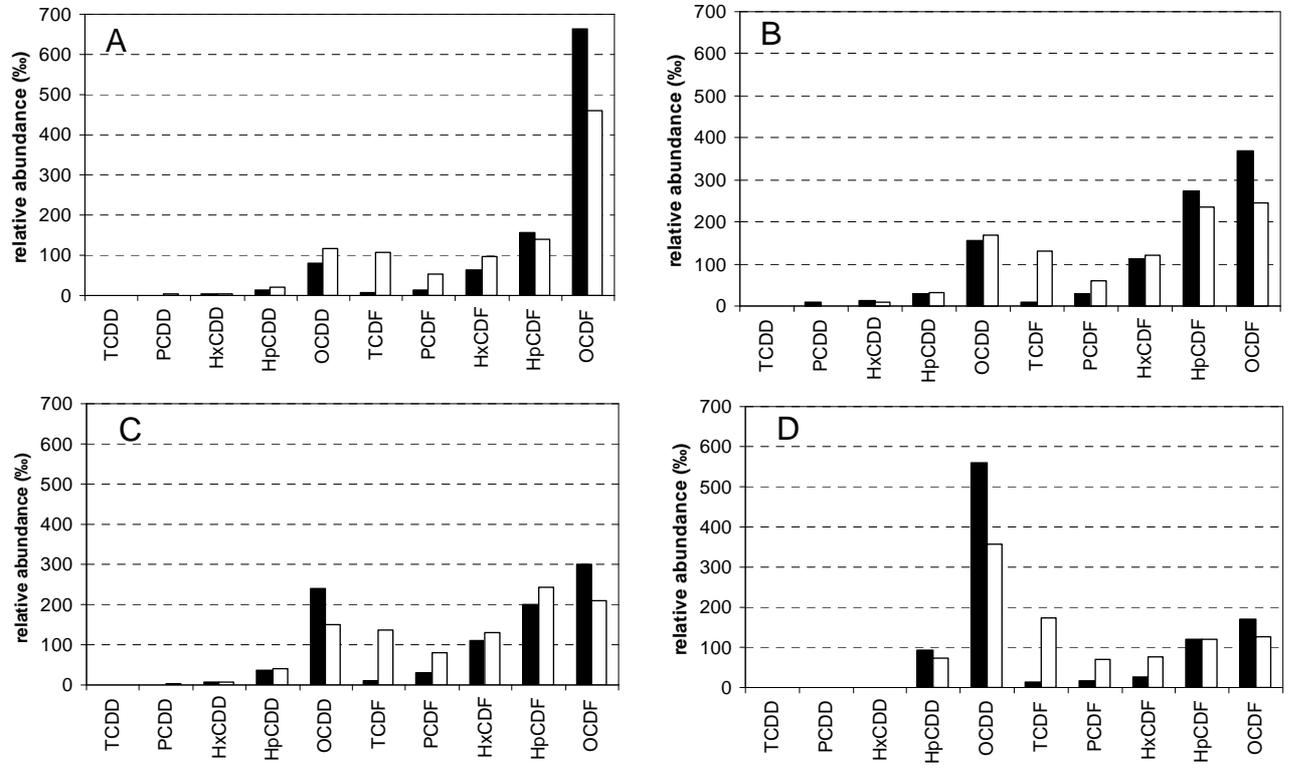


Figure 5



## Figure captions

Figure 1: Map of Lagoon of Venice with locations of atmospheric bulk deposition (triangles: DOG, EZI, IBM, L1, L2, L3) and water sampling sites (squares, “a” to “r”). Open circles: surface sediment and *Tapes philippinarum* sampling areas. Dotted line subdivides inner (west) from outer (east) lagoon described in text. Cross-hatched areas: industrial zone of Porto Marghera (left) and city of Venice (right).

Figure 2: Map of values of Integrated Enrichment Factors (IEFs), calculated by summing ratio of surface sediment values of PCB, PCDD/Fs and HCB, divided by respective background values (see text for explanations). POP data of bottom sediments (filled dots) derive from various papers (Marcomini et al., 1999; MAV-CVN, 2000; Bernstein et al., 2002). Open circles (A to D): fishing and harvesting areas where clams and sediments were sampled concurrently.

Figure 3: Differences between overall values of PCDD/Fs at various points (dimension of dots is proportional to concentrations) and examples of fingerprints from three subareas (separated by full lines): (i) industrial zone (station D), (ii) city of Venice (station B), and (iii) remote southern lagoon areas (station I).

Figure 4: Regression ( $r^2 = 0.57$ ) between logarithm of I-TE in clam flesh (dependent variable) and sediment (independent variable), concurrently sampled in same sites.

Figure 5: Comparisons between PCDD/F fingerprints in sediments (black bars) and clams (white bars). A = industrial zone, B = northern lagoon, C = central lagoon, D = southern lagoon.