FATE OF PERSISTENT ORGANIC POLLUTANTS IN THE VENICE LAGOON: FROM THE ENVIRONMENT TO HUMAN BEINGS THROUGH BIOLOGICAL EXPLOITATION?

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Abstract. The Lagoon of Venice has been receiving discharges of many classes of persistent organic pollutants (POPs) that have been accumulating in sediments and marine organisms and might represent an indirect threat to human health. In particular, the intensive harvesting of Manila Clam (*Tapes philippinarum*) and other traditional fishing activities carried out in the lagoon represent the highest direct source of risk for human health. This paper presents an overview of sources and fates of dioxins, polychlorinated biphenyls and hexachlorobenzene in the Lagoon of Venice. Pollution data of environmental matrices (atmospheric depositions, water and sediments) and biota (clams) of the lagoon are presented for describing the environmental and biological contamination. Evidences on possible human contamination are derived from recent data of POPs in mother milk and blood serum of Venetians with different work exposure and food habits. This overview evidences a critical environmental state for some areas of the Venice Lagoon and confirms a non-negligible human health risk for regular shellfish and fish consumers. The overview supports the need for keeping some lagoon areas restricted to fishing and for maintaining the current situation under monitoring.

Keywords: POPs, dioxins, polychlorinated biphenyls, hexachlorobenzene, monitoring.

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1. Introduction

Despite regulations and monitoring programs coastal areas are inevitably receiving organic pollutants that are waste products of industrial and other human activities in the mainland. In particular, the persistent organic pollutants (POPs), that are characterized by low degradation rates and high affinity to lipids and organic matter, accumulate in coastal sediments. Therefore, POPs might be available directly to benthic species and then indirectly transferred to other organisms of the food web even several years after their discharge to the environment. Human beings, through the exploitation of coastal resources, are the top predators of marine coastal food web and thus, other than the producers, are the final receptor of these pollutants [15]. In degraded situations the fishery exploitation and consumption of seafood might enhance human health risks that need to be considered as a further critical effect of POPs and included in the ecosystem health assessments [12].

In this work the case of the Lagoon of Venice (Italy) is presented that has been receiving discharges of many classes of pollutants, including POPs [3]. This ecosystem is also providing several services to local population, including traditional fishing activities and intensive exploitation of Manila Clam (*Tapes philippinarum*). Despite the many possible fates of POPs in this system, these exploitation activities might represent the highest direct source of risk for human health. Here, an overview of sources and fates of dioxins, polychlorinated biphenyls and hexachlorobenzene in the Lagoon of Venice are presented, using the data regarding contamination of environmental, biological and human matrices.

2. The Lagoon of Venice

The Lagoon of Venice (Adriatic Sea, Italy), is the largest lagoon in the Mediterranean Sea. It covers an area of about 500 km^2 and has an average depth of 0.7 m. The lagoon is characterized by large shallow areas divided by a network of deeper channels connected to the Adriatic Sea by three narrow inlets that allow seawater circulation. Thus, these features result in a complex geomorphological, hydrodynamic, and ecological system.

In the last century an industrial pole on the lagoon shores has been developed into one of largest industrial areas in Europe: the Industrial Zone of Porto Marghera. Here, a very broad range of activities and processes like non-ferrous metal production, chemical industry, municipal, hospital and hazardous waste incineration have been important sources of dioxins and dioxin-like compounds as well as other classes of pollutants that were released into the environment [3,4]. Moreover, discharges from urban areas (mainly cities of Venice, Chioggia and Mestre), diffuse pollution in the watershed basin, sewage treatment plants, leakage, and incomplete fuel combustion from boats represent secondary sources of POPs to the lagoon.

The Lagoon of Venice is also an ecologically important saltmarsh environment being a wintering site for seabirds [1] and nursery area for many fish species [13]. Natural resources of this productive ecosystem are exploited since centuries by traditional fishing and farming activities producing between 3,000–6,000 t $year^{-1}$ of fish in the last decades. Moreover, the benthic bivalve Manila Clam (*Tapes philippinarum*) was introduced in the 1980s and subsequently a mechanical clam harvesting activity was developed, exploiting the entire central part of the lagoon and providing the fish market with up to 40,000 t $year^{-1}$ of clam, i.e., more than 50% of the Italian clam production [6]. Despite that the clam harvesting is not allowed nearby the Industrial Zone, the contaminated clams are illegally caught in this highly polluted area, and fish indirectly contaminated by food web accumulation [2] might reach the consumers and represent a direct source of risk for human health.

3. Environmental contamination

Monitoring of POPs in several sampling stations in the Lagoon of Venice have been carried out in the last decade for evaluating the contamination of different environmental matrices, thus including the fall out, water column, and sediments (see Fig. 3.1).

3.1. Atmospheric depositions

In a study conducted in 2002–2003, 58 samples of atmospheric depositions were collected using bulk samplers placed in seven stations located in different areas of the lagoon [14]. Average daily depositions of PCB, PCDD/F and HCB in stations around the industrial area resulted in 13,669, 278 and 2,297 pg m^{-2} d^{-1}, respectively, and toxicity equivalent to 6.5 pg I-TE m^{-2} d^{-1}. For comparison, daily depositions in the city of Venice were on average 1,348, 35 and 247 for PCB, PCDD/F and HCB, respectively, and toxicity equivalent to 0.9 pg I-TE m^{-2} d^{-1}. In general, depositions of POPs in industrial area were one order of magnitude higher than in other stations.

The comparison of the results of the study conducted in 2002–2003 with fallout estimated for 1998–1999 evidenced a decrease of PCB and HCB depositions but toxicity remained high because of important contribution from PCDD/F. In fact, toxicity of PCB and PCDD/F deposition was calculated as 233 and 280 mg I-TE yr^{-1} for 1998–1999 and 2002–2003 samples, respectively [14]. The results showed that the industrial area is still an important source of atmospheric depositions containing POPs. These findings were confirmed by the new data collected in 2004 [5].

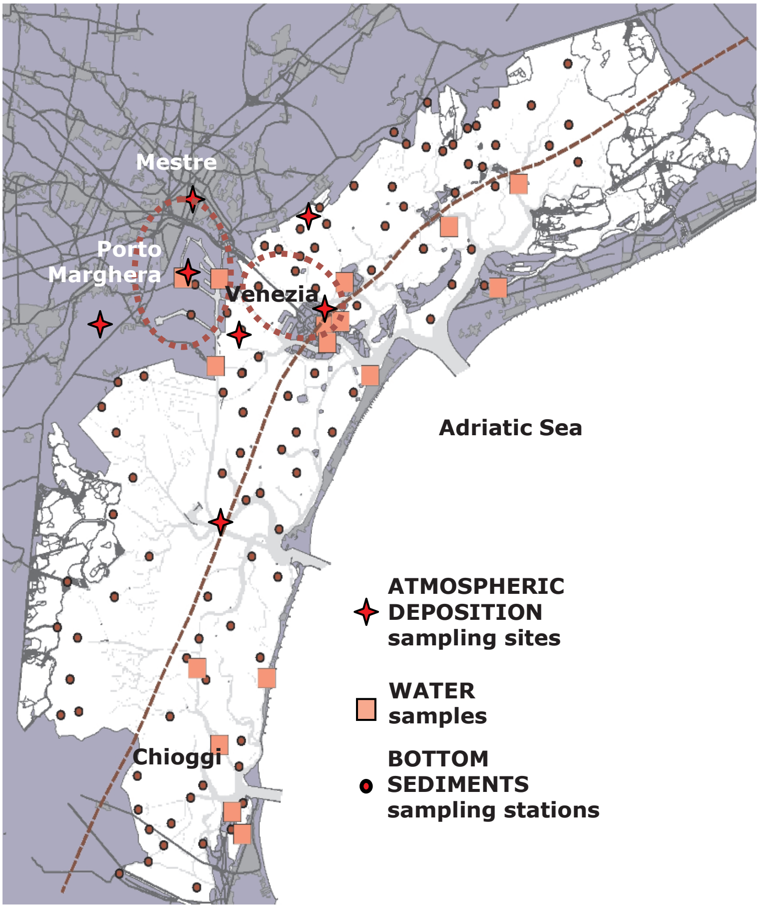

Fig. 3.1. Sampling stations for POPs' monitoring in the Lagoon of Venice.

3.2. Water column

In a study conducted in 2001, water samples were collected monthly in 16 stations of the lagoon [7]. Average concentrations in lagoon waters of PCB, PCDD/F and HCB were reported as 0.3 ng l^{-1}, 2 pg l^{-1} and 0.03 ng l^{-1}, respectively. Water of industrial channels resulted in having concentrations one order of magnitude higher, i.e., 2.1 ng l^{-1}, 17 pg l^{-1} and 0.27 ng l^{-1} for PCB, PCDD/F and HCB, respectively. However, also the water of canals in the city of Venice showed high concentrations 2.6 ng l^{-1}, 12 pg l^{-1} and 0.09 ng l^{-1}, respectively, providing evidence of non-negligeable secondary sources of these pollutants from urban area. In terms of toxicity, in fact, the industrial area was the most important source (0.36, 0.26, 0.05 pg I-TE l^{-1} for industrial channels, city canals, and lagoon, respectively).

3.3. Sediment contamination

In spite of water circulation, the lagoon sediments represented the main sink for POPs and today constitute the main burden of PCDD/F, PCB, and other persistent organic pollutants. Since 1997 several studies have been carried out for measuring concentrations of POPs in superficial sediments (0–15 cm) at different sites of the lagoon (see Fig. 3.1). Average values of POPs concentrations in sediments of homogeneous areas of the lagoon have been compared with background concentrations measured in core samples. In sediments of industrial channels, results evidenced concentrations of 810, 14 and 260 μg kg^{-1} dw for PCB, PCDD/F and HCB, respectively (dw = dry weight). Outer lagoon was much less contaminated with concentrations of 5, 0.3 and 0.2 μg kg^{-1} dw, respectively. However, the comparison is even more critical when background pre-industrial levels are used, i.e., 0.001, 0.03 and 0.1 μg kg^{-1} dw. Although the sediment contamination of Venice canals was quite high (PCB = 600 μg kg^{-1} dw; PCDD/F = 0.5 μg kg^{-1} dw), the results evidenced the industrial area as the primary source of POPs discharges in the Lagoon of Venice ecosystem. Moreover, the sediments of the industrial channels presented the toxicity three orders of magnitude higher than background values and two orders higher than outer parts of the lagoon [5].

These data represent a quite robust description of the POPs contamination of the lagoon and evidenced the maxima of concentrations in the channels around the industrial area. In particular, the superficial sediment concentrations of POPs with a toxicity higher than 2,500 ng I-TEQ kg^{-1} dw can be found in the channels of the industrial area. Moreover, the integrated enrichment factors, calculated on the basis of ratio between the actual and background concentrations of POPs, clearly evidenced the hot spots of pollution in the inner-central part of the lagoon around the industrial area of Porto Marghera [5].

Moreover, the PCDD/F fingerprints in the sediments of different areas were compared with those of the industrial and urban wastes (sewage treatment plant), showing clearly that these hot spots are related with the discharges and wastes from the production of dichloroethylene (DCE) and vinyl chloride (VCM) for PVC production.

4. Contamination of biota

The high contamination of lagoon sediments in certain areas is a source of serious concern for the possible bioavailability of POPs to the benthic community and their entering into the lagoon trophic chain [2]. In particular, due to its intense exploitation and its strict benthic ecological properties, Manila Clam (*Tapes philippinarum*) is the most studied species in terms of contamination with POPs [8–11].

4.1. Contamination of Manila Clam

Several POPs data for both sediments and Manila Clam evidenced that sediments are the major direct source of contamination for this benthic bivalve. Moreover, dioxin fingerprints for both sediments and clam flesh highlight the main source of POPs for different areas of the lagoon [5].

The ranges and the average values of the toxicity equivalent in the clam flesh in the three monitoring area in the northern, southern and central part of the lagoon has been compared with those concerning the clam sampled nearby the industrial area [11]. PCDD/F and PCB concentrations expressed in toxicity equivalents were quite similar in the three fishing areas (0.2 pg WHO-TE g^{-1} ww; ww = wet weight) and were approximately an order of magnitude lower than those found in the canals of the industrial zone (2 pg WHO-TE g^{-1} ww), where the fishing is forbidden. However, it is worth noting that concentrations up to 9 pg WHO-TE g^{-1} we have been found in flesh of clams collected in the industrial channels [11].

The relative concentrations of the main dioxin congeners in both sediment and clams strongly suggest that the sources of contamination in the three monitored areas are different. In fact, the fingerprint concerning both the sediment and the clams nearby the industrial area was characterized by the highest percentage of OCDF. The percentage of OCDF was lower in the other three areas and reached its minimum in the South Lagoon, where the fingerprint was characterized by the highest percentage of OCDD, which is usually found in the discharges of urban waste water treatment plants and can be released into the environment also by combustion processes and boats engine [11].

This finding indicated that the central and north lagoon was affected by both urban wastewater and industrial pollution. However, the higher OCDF percentages with respect to OCDD in the industrial area suggest that the contamination is related, directly or indirectly, to industrial activities. Interestingly, the dioxin fingerprints for clam and sediment pertaining to the same area were remarkably similar: This finding supports the hypothesis that the sediment is still the main source of contamination for clam and suggests the presence of a quantitative relationships between the equivalent toxicities in the abiotic and biotic compartment.

In this framework a regression model between sediment and clam's toxicity has been identified as a valuable tool for health risk assessment [8]. In fact, the regression between the logarithms of the WHO-TE in clam flesh and sediment was found to be statistically significant for both PCDD/F and PCB.

This prompted the development of experiments consisting in the displacement of clam from a polluted to a cleaner area for allowing natural detoxification from POPs [8,10]. The results evidenced the high detoxification rates, and a bioaccumulation model provided basis for estimating the capabilities of clam to detoxify [10]. The findings all concur in evidencing that clams contaminated by industrial pollution underwent a very rapid decline of TE when the specimens were harvested and transplanted into the areas with low contaminated sediments. This culture-based fishery regime might represent a possible solution for avoiding an incidental direct human exposure to dioxins and PCB through contaminated clams reaching the fish market.

5. Human contamination

Although the overview of environmental and biological POPs contamination might evidence the possible sources of these pollutants to human beings through air, water and food, it is difficult to evaluate and control these sources. Direct and indirect sources of POPs were assessed in order to test the possible human contamination, and recent data on mother milk and on blood serum of Venetians with different work exposure and food habits were compared with other sources.

5.1. Blood serum

In a recent work, two datasets on POPs concentrations in serum referred to Italian men with different exposure histories were presented and compared [8–10]. One dataset, collected in 1998 and particularly focusing on dietary exposures, regarded the determination of PCB and PCDD/F in blood serum of 41 selected volunteers, was divided into two groups: 22 consumers eating large amounts of locally caught fish and shellfish, and 19 people consuming very little fish of any kind. The second dataset represents the concentrations of PCB, PCDD/F and HCB in serum samples collected in 2007 and refers to 16 Italian volunteers with diverse exposure histories: Six individuals have been employed for several years in chemical plants of Porto Marghera Industrial Zone, whereas for the other ten people no particular concerns regarding their exposure life histories are known [9]. The results obtained are compared in Figs. 5.1.1–5.1.3 for PCDD/F, PCB and HCB respectively.

Results for PCDD/F (Fig. 5.1.1) show an average toxicity of 13.91 and 19.33 pg TE g^{-1} lipid for low ($n = 19$) and high fish consumers ($n = 22$), respectively; whereas values of 16.08 and 9.41 pg TE g^{-1} lipid were found for individuals subjected to occupational exposure ($n = 6$) and for the others with unknown exposure life-histories ($n = 10$), respectively.

The results for PCB concentrations in blood serum (Fig. 5.1.2) show a significant difference between low and high fish consumers with averages of 9.30 and 30.68 pg TE g^{-1} lipid, respectively; whereas the average values of 22.00 and 6.77 pg TE g^{-1} lipid were found for occupational exposed and the others, respectively. On the basis of these results [9] concluded that total PCB TE values are significantly different either between the groups with different dietary habits (low and high fish consumers) and between the groups distinguished on the basis of occupational or general exposure. Moreover, PCBs TE values for high fish consumers in Venetian population are comparable with the values of the group of people subjected to workplace exposure. The data for HCB concentrations (Fig. 5.1.3) evidenced the sensible difference between the concentration in blood serum of males subjected to workplace exposure (0.073 µg HCB g^{-1} lipid) and to general exposure (0.023 µg HCB g^{-1} lipid).

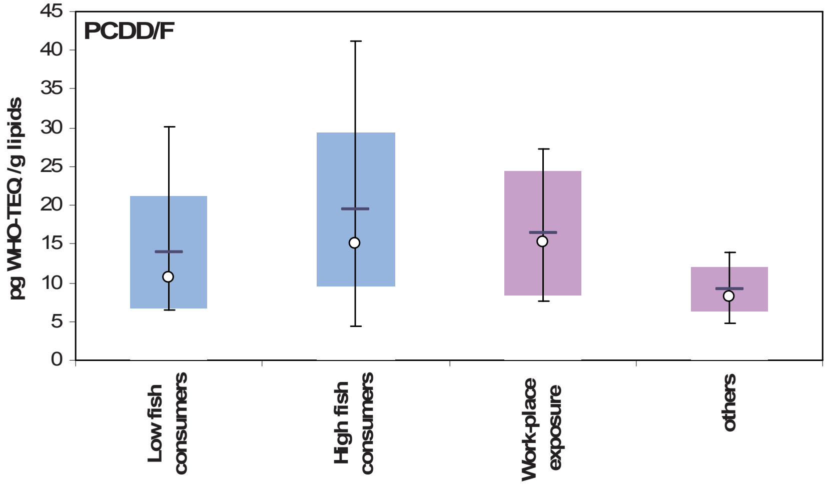

Fig. 5.1.1. PCDD concentrations in blood serum.

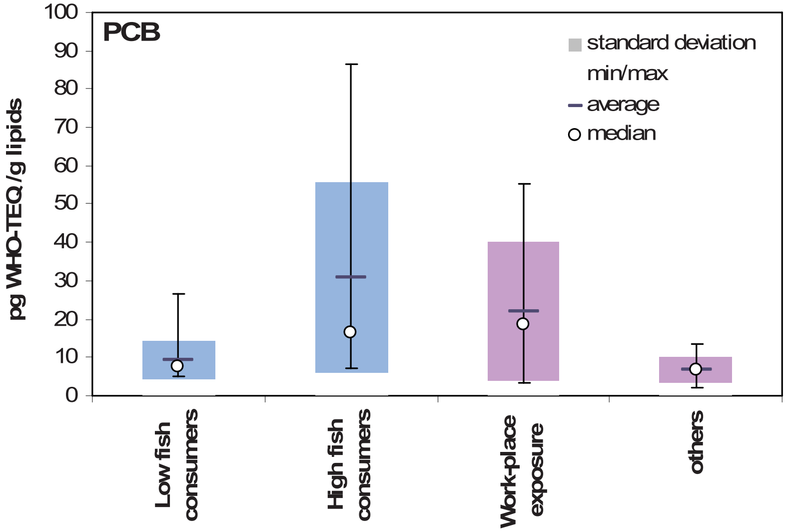

Fig. 5.1.2. PCB concentrations in blood serum.

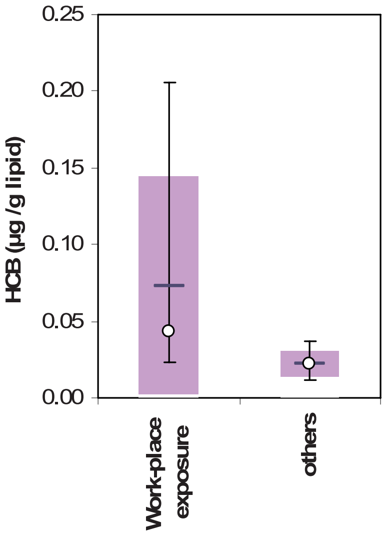

Fig. 5.1.3. HCB concentrations in blood serum.

Precaution is recommended considering these evidences because of the limited number of the samples. Nevertheless, these results support the concerns regarding the human exposure to dioxins and claim for further epidemiological studies in order to provide a deep insight into the exposure levels for the Italian population.

5.2. Breast milk

New data of POPs in the breast milk were measured in 2008 of 3 mothers living in Venice. The averages were resulted in 5.2 ± 1.7 pg WHO-TE g^{-1} lipids for PCDD/F and 6.7 ± 1.3 pg WHO-TE g^{-1} lipids for PCB. Total toxicity of PCDD/F + PCB was, therefore, 11.9 pg WHO-TE g^{-1} lipids. Analogous analyses conducted in 2000 for Venice and Rome resulted in 30.7 and 20.4 pg WHO-TE g^{-1} lipids in average, respectively.

Therefore, the results obtained in 2008 for WHO-TE are lower than those measured in 2000 but some caution is required in giving any conclusion because of the small number of 2008 data (three cases). In fact, the comparison with the data available in literature [15] shows that the collected data are in the upper part of the variability range presented in literature, and the comparison with the similar data collected in 2000 shows the higher contamination in the breast milk of mothers from Venice than at the mothers from Rome.

6. Conclusions

The fall-out, water and sediment data show very high concentrations of POPs, mainly in the industrial area of Porto Marghera and its surroundings. Thus, the industrial sources appear clearly as the main POPs sources in the Lagoon of Venice whereas the city of Venice and other urban areas appear to be of secondary importance.

The direct discharges continue to be a major POPs source to the environment, and atmospheric fall-out can be a secondary source. In particular, the data show a decrease of POPs in atmospheric depositions but the fall-out continues to play a substantial role to the inputs of POPs in the lagoon.

POPs are clearly accumulated in the sediments of the lagoon, with concentrations in industrial channels that are three orders of magnitude higher than the background values, while the other parts of the lagoon show concentrations, which are 5–10 times above the pre-industrial levels. The dioxin fingerprints evidenced that sediment is the main source of contamination of clams by the industrial-derived dioxins. There are high concentrations of POPs in the clams fished in the industrial channels.

A little enrichment (although not significant) of PCDD/F human blood serum could be linked to the fish consumption and occupational exposures of Venetian volunteers. On the contrary, considering total PCBs toxicity, the higher values for Venetians are clearly associated with the high fish consumers and the workers of chemical plants of the Venice Lagoon. The preliminary studies on human contamination presented here, although based on a limited number of samples, are supporting the concerns regarding the human exposure to dioxins and claim for further epidemiological studies in order to provide a deep insight into the exposure levels for Venetian and Italian population. Moreover, the higher levels of PCDD/F and PCB are found in the breast milk of Venetian mothers compared with the Roman ones in 2000. Although the toxicity levels in the breast milk in 2008 are lower than those measured in 2000, drawing more robust conclusions ask for a larger number of investigated cases.

There is a clear need for a constant monitoring of POPs in the Venice Lagoon in order to let this fragile ecosystem to heal gradually its wounds, and to safeguard it from further pollution. The environmental monitoring is indispensable for giving information about ecological risks.

This overview evidences a critical environmental state for some areas of the Venice Lagoon and confirms a non-negligible human health risk for regular shellfish and fish consumers. In general, this overview supports the need for keeping some lagoon areas restricted for fishing and for maintaining the current situation under the monitoring.

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