

Selected persistent organic pollutants (POPs) in the Italian environment

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Summary. - The ratification of the Stockholm Convention on Persistent Organic Pollutants is a departure point for several considerations on their presence in environmental matrices. In this paper, the Italian situation is presented with emphasis on the most toxic compounds - chemicals with dioxin-like toxic action, and the activity in the area of interest of the Istituto Superiore di Sanità. Biotic, as well as abiotic matrices have been taken in consideration and, where possible, a comparison between their contamination levels with the levels reported on similar matrices by other European countries has been reported.

Key words: Stockholm Convention, persistent organic pollutants, sediments, soil, biota.

Riassunto (*Contaminanti organici persistenti nell'ambiente italiano*). - La ratifica della Convenzione di Stoccolma sui contaminanti organici persistenti costituisce il punto di partenza per svariate considerazioni sulla presenza di questi xenobiotici nelle matrici ambientali. In questa breve rassegna viene presentata la situazione italiana ponendo l'enfasi sui composti più tossici del suddetto gruppo - quelli ad azione diossina-simile - e l'attività dell'Istituto Superiore di Sanità in quest'area d'interesse. Sono state prese in considerazione sia matrici abiotiche sia matrici biotiche e, ove possibile, è stata effettuata una comparazione tra i loro livelli di contaminazione con i livelli riportati per le stesse matrici in altre nazioni europee.

Parole chiave: Convenzione di Stoccolma, contaminanti organici persistenti, sedimenti, suolo, biota.

Introduction

Due to the enacting of the Stockholm Convention on Persistent Organic Pollutants (POPs) on 17 May 2004, we deemed of interest the data on their presence in Italian environmental matrices. The Stockholm Convention establishes the immediate banning of most of the 12 POPs initially individuated (aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, mirex, toxaphene, PCBs, HCB, PCDDs, and PCDFs) [1].

Since the Seveso accident in 1976, the Italian National Institute of Health (Istituto Superiore di Sanità, ISS, Rome, Italy) has been involved in a large number of initiatives to monitor, assess, and manage the risk associated with several persistent organic pollutants (POPs). The group of chemicals usually investigated includes: polychlorinated biphenyls (PCBs), dibenzodioxins (PCDDs), and dibenzofurans

(PCDFs), some chlorinated pesticides (hexachlorobenzene (HCB), *p,p'*-dichlorobiphenyltrichloroethane (*p,p'*-DDT), *p,p'*-dichlorobiphenyldichloroethylene (*p,p'*-DDE)), and a selection of polycyclic aromatic hydrocarbons (PAHs). Many of these initiatives appear to reflect critical situations (e.g., the ACNA chemical plant at Cengio (Savona), the anthropogenic impact on the Venice lagoon, the "Belgian crisis" of food contamination, several chemical plant fires): they could be qualified as "institutional." Other actions stemmed from well-planned research studies and properly belong to the scientific domain.

In this report essentially two items have been taken in consideration in dealing with the levels of POPs in Italian abiotic and biotic matrices: 1) the levels of "dioxins" (PCDDs and PCDFs) and chemicals with a dioxin-like toxic action in abiotic and biotic matrices, and 2) some activities in the area of interest of the ISS.

Levels in abiotic matrices

Soil

An investigation carried out in the early '90s was planned to determine PCB, PCDD, and PCDF background levels in the general environment in Italy in topsoil samples [2]. The items considered were: (a) the distribution pattern of the chemicals as a function of sampling site location, (b) the analytical patterns of PCDD and PCDF congeners and selected PCB homologs per type of sampling location, (c) to verify whether a correlation existed between the cumulative levels of PCBs and those of PCDDs+PCDFs I-TEQ values [2]. Sampling was carried out in five Italian regions (Abruzzi, Latium, Liguria, Piedmont, and Tuscany). Samples of topsoil (upper 10-20 cm) were collected at sea level or slightly above this level, at an altitude of 800-1300 m, and in caves usually not visited by common people. Particular attention was given to selecting sampling sites far away from large urban or industrial settings, at least 5 km away from towns and villages, in unfarmed fields, and possibly in wild areas. On the whole, 28 samples were collected and analyzed.

Cumulative PCB levels ranged 6.2×10^2 to 1.6×10^4 ng/kg of dry matter (dm) in open areas and 1.2×10^2 to 6.8×10^2 ng/kg dm in cave samples. PCDDs+PCDFs covered a range of 1.0×10^{-1} to 4.3 ngI-TE/kg dm in open areas and of 5.7×10^{-2} to 1.2×10^{-1} ngI-TE/kg dm in cave specimens. Both Student's t-test and the Mann-Whitney test failed to prove any differences between data distributions of sea level and altitude samples. However, a significant difference was detected between cave samples and the others. On the basis of PCB analytical pattern, it was shown that the less chlorinated PCB homologs reached higher relative levels in cave sediments than in topsoil samples, probably because in a protected environment their dissipation rate was lower. PCDDs and PCDFs patterns of topsoil and cave samples could not be properly compared due to the preponderant number of "not determined" in cave matrices. In addition, the highly significant correlation found between the cumulative PCB (ng/kg dm), and PCDD+PCDF (ngI-TE/kg dm) levels showed that local important sources of contamination were absent [2].

Sampling sites selected for this study, as mentioned before, were far from direct contamination sources. Therefore, it appears correct to compare our data with those produced in other studies related to background European areas. Soil background levels determined in southern European countries (Spain, France, and Greece) range was 0.02-2.24 ngI-TE/kg dry weight (dw) [3] therefore, concentration levels reported for the Italian general environment appear, in open areas as well as in caves, in agreement with the range reported.

Aquatic sediments

In the early 1990s, the Italian National Institute for Health set out a number of studies to characterize the Venice lagoon contamination. There was a specific focus on several heavy metals and a number of persistent organic pollutants selected from the chemical families of PAHs, PCBs, PCDDs and PCDFs, and some chlorinated pesticides. Over the years, the work received additional financial support from the Ministry for the University and Scientific Research, the State Attorney-General Deputy in Venice (within the framework of a specific investigation), the Ministry of the Environment, and the Veneto Regional Board. In addition, the burden of the aforementioned chemicals in marine food from the lagoon was also examined in response to a request by the Ministry of Health.

The preliminary contamination scenario obtained from the assay of sediment samples showed a strong correlation between contamination and anthropogenic impact (Table 1). This led to a pragmatic subdivision of the lagoon and the neighboring Adriatic Sea in six virtual areas of toxicological risk as shown in the Table. Some examples of PCDD+PCDF contamination levels of sediment and biota samples belonging to the same areas, as well as some results of the PRISMA 2 Project, have been reported [4]. The subdivision was based on locally presumed - and later confirmed - relevant anthropogenic impacts. The data obtained and under acquisition will be used to outline low resolution contamination scenarios and to suggest measures for risk reduction and risk management practices, in order to protect human health with a cost-to-benefit approach.

In the lagoon, sediment contamination magnitude spans from the higher levels of virtual area 1 (industrial or prevailing industrial exposure) and area 2 (urban or prevailing urban exposure) to the lower values exhibited by the fishing zones of area 4, 5 and 6 (the last two are not shown in Table 1). With reference to the 66 top sediment samples analyzed, the PCDD+PCDF value ranges in the six areas were found to be (area, pgI-TE/g dm): area 1, 1.0-1300; area 2, 4.8-23; area 3, 0.48-30; area 4, 0.24-3.3; area 5, 0.72-3.2; area 6, ≈ 0.07 -17 [5, 6].

All the results were subjected to cluster analysis (K-means method) to confirm the areas' preliminary classification (see above). Three-cluster grouping appeared to segregate samples according to the presumed impacts, showing a prevailing presence of samples (sediments) collected in virtual areas 1 and 2, respectively, in clusters 1 and 2. Whereas cluster 3, notable for the definition of background values, included all the remaining samples characterized by less defined impact(s) and, in general, low contamination levels. In this cluster, samples from areas 4 and 5 were included, far from direct contamination sources [7].

Table 1. - Synoptical comparison of organic contamination levels in the Venice lagoon virtual risk AREAS 1, 2, and 4, and in mussels, clams and other biota samples collected in different sampling campaigns

	Analyte levels (ng/g, whole weight, except where noticed)					
	PAHs	PCBs	PCDDS+PCDFs		<i>p,p'</i> -DDE	HCB
			pg/g	pgI-TE/g		
AREA 1 - Industrial or prevailing industrial exposure						
Sediments	≈40-93000	2.4-55000	54-430000	1.0-1300	0.15-65	2.5-800000
Biota	62-220	23-180	73-45	0.78-5.3	0.82-39	4.0-18
AREA 2 - Urban or prevailing urban exposure						
Sediments	360-48000	~20-790	210-1400	4.8-23	0.19-27	0.33-9.0
Biota	26	29	13	0.87	1.2	0.73
AREA 4 - Low exposure, open fishing areas						
Sediments	≈5-220	0.27-9.8	5.0-160	0.13-1.1	<0.05-1.3	<0.05-0.29
Mussels	5.2-17	14-46	3.1-7.6	0.23-0.68	1.5-3.8	<0.08-0.55
Clams	2.8	1.9	1.4	0.079	0.18	0.29
ADRIATIC SEA (Prisma 2 Project)						
Mussels	-	6.7-45	1.4-3.1	0.11-0.24	1.6-3.0	-
Clams	-	3.7-10	0.76-1.9	~0.07-0.13	~0.7-~0.8	-

Twenty-four samples from different sites and depth were analyzed to study the vertical distribution of contaminants. In virtual area 1 the deep sediment layers exhibited contamination levels greater than those detected in the corresponding top layer specimens. In particular, for PCBs and PCDDs+PCDFs the concentration increase hits between one and two orders of magnitude; for HCB, an increase of up to three orders of magnitude was observed. However, distribution patterns were found to be largely analyte- and site-specific [8].

Some observations can be drawn from the results obtained from cluster analysis: (a) in the Venice lagoon, the chlorinated compounds (in particular, PCDDs+PCDFs and HCB) qualify as probably the best tracers of (historical) industrial activity, and (b) the relative high contamination levels detected in the deeper sediment layers at two industrial (virtual area 1) sites are likely to date back to years ago, when contamination releases were greater than at present.

In the Mediterranean region PCDD+PCDF levels have been reported for sediments of the Catalan coast, as determined in the late '80s and early '90s [3]. The concentration levels ranged approximately 0.4-8 ngI-TE/g dw whereas, under the influence of sewage sludge, concentrations increased to 57 ngI-TE/g dw. High HCB individual concentrations were found in sediment samples from Rhone and Ebro Prodeltas where 39 and 19 ng/g (dw) were found, respectively [3].

Levels in biotic matrices

Venice lagoon and Adriatic Sea

The Venice lagoon biota, obtained at or near the locations where sediments were sampled (see above), in general showed a trend towards higher contamination levels with increasing anthropogenic impact, that is moving from virtual area 4 to area 1 (Table 1) [9, 10]. For

mussels, in the areas shown in Table 1, a range of PCDD+PCDF values of 0.68-4.9 pgI-TE/g, whole weight (ww) was detected. In particular, the amount of PCDDs+PCDFs found in mussels from area 4 (within the lagoon) did not appear to be significantly different from that found in mussels collected in breeding areas along the Italian Adriatic coast (0.11-0.24 pgI-TE/g, ww) [4]. However, it is presumed that these mussels, sampled in areas suitable for bivalve cultivation, are not directly exposed to a chemical anthropogenic impact.

For risk management aims, the determination of environmental background levels is a key issue. The background statistical values for PCDD+PCDF in mussel and clam organisms from the Venice lagoon have recently been described by Miniero and co-workers [11]. Clam background values considered resulted from three to five times lower than the values of mussel background, with respective means of 0.1 and 0.44 pgWHO-TE/g ww [11]. The background values indicated are in agreement with those of open Adriatic sea breeding areas [4].

As indicated above, mussels of the Italian Adriatic coast were also analyzed in another study [4]. Particularly, this was carried out with various edible species with the aim to estimate the extent of PCB, PCDD+PCDF, *p,p'*-DDE, *p,p'*-DDT, and HCB contamination in fish products from different areas of the Adriatic sea. The marine species selected had a high commercial value and were obtained from fishing harbors situated in the northern (nine sites), central (six sites), and southern (four sites) Adriatic sea. On the whole, PCDD+PCDF contamination appeared to be low. In general, the findings were greater for those species at higher levels in the trophic web (mackerel, 0.59-1.1 > red mullet, 0.37-0.56 > anchovy, 0.23-0.47, all in pgI-TE/g ww), although the higher fat content of some species appears to take account for part of the contamination measured. With some exceptions, PCDF analytical contribution was greater than that of PCDDs; in addition, the cumulative I-TE findings were greater in species from the northern harbors than in those sampled in the central and southern Adriatic sea. Accordingly, PCB

contamination revealed a remarkable difference between the three areas; the northern site specimens resulted more contaminated than the central and southern ones (10.3-177 > 5.55-157 > 3.72-94.1, in ng/g ww). As expected, contamination appears to change according to the trophic level considered, with the mackerel being the species more contaminated and with higher fat content [4].

Predators and cetaceans

It is of interest to report concentration data also for organisms like cetaceans and predators, such as sharks and tuna, sampled along the Italian coast, for their position in the food web. However, it should be highlighted that PCDD+PCDF determinations in Mediterranean biota are rare.

In the blubber (a subcutaneous lipid reservoir containing an approximately 35-40% fat) of the dolphins *Tursiops truncatus* and *Grampus griseus* found stranded along the Italian Adriatic coast in 1992, concentrations of respectively 19 and 21 ngPCB-TE/g ww were found [12, 13]. These levels have been reported in toxic equivalents derived from the TEF system developed by Safe [14] for dioxin-like PCBs, and do not include the contribution from PCDDs and PCDFs. Concentration values were also reported for the blubber of dead cetaceans specimens and result approximately two orders of magnitude higher than those measured in the brain [15, 16]. Several factors, such as the physiological state of the organism and the tissue considered, including the TEFs system adopted, appear to influence the total levels reported. However, one of the most important parameter that influences the tissue-specific body-burden determinations can be the mobilization of lipid reservoirs occurring during starvation [17]

In the fat of shark species *Prionace glauca* and *Rapias vulpinus* collected during 1992 in the south Adriatic sea areas [12] (S. Maria di Leuca and Porto S. Giorgio, respectively) non-ortho PCBs were found to range from 2.7 to 240 pgTE/g ww [12]. In the muscles of two other shark species - the gulper shark,

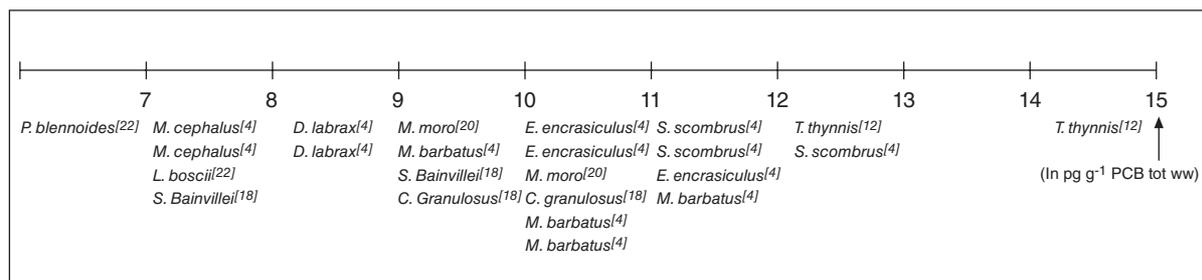


Fig. 1. - Total PCB estimates in muscles or in total body of Mediterranean fish species. Values reported as ln[PCBTOT], in pg g⁻¹ whole weight (ww).

Centrophorus granulosus, and the longnose spurdog, *Squalus bairdii* - also caught in the south Adriatic sea between June and August 1999, the TEQ concentrations are situated at the lower end of the previous range. Much higher levels were present in the liver and eggs (respectively, 200 and 100 pgTE/g ww for *C. granulosus*, and 170 and 45 pgTE/g ww for *S. bairdii*) [18]. However, in addition to cartilaginous species, fish of high commercial value, such as the bluefin tuna, *Thunnus thynnus*, have been analyzed. A concentrations range of 17-200 pgTE/g ww [12] was found in the muscles of this fish collected in the Egadi Islands near Sicily (May 1993).

Some papers report POP levels other than those of chemicals with dioxin-like toxic action in aquatic organism tissues. In aquatic mammals, in particular the striped dolphins *Stenella coeruleoalba*, sampled in the Ligurian and Tyrrhenian seas in 1991-1993, and in the fin whales *Balaenoptera physalus*, collected during the summer of 1990-1993 in the Ligurian Sea, higher chlorinated PCBs have been found. The hexachlorobiphenyl (H₆CB) and heptachlorobiphenyl (H₇CB) homologs prevail over the other PCBs present in the mixture, PCBs 153, 138, and 180 being the most abundant congeners [13, 19]. In particular, the hexachlorosubstituted PCB 153 shows the highest concentration in the blubber, 14 µg/g, lipid base (*lb*) [13]. The congener prevalence found in marine mammals was also found in both surficial and deep-sea Mediterranean fish [12, 20, 10]. In top level predators, like tuna and shark, the relative concentration of PCB 153 reaches, respectively, 160 and 330 ng/g ww. In Fig. 1 the range of total PCB estimates found in muscles or total body samples from Mediterranean fish has been reported as ln pg[PCBs]g⁻¹ ww. As expected, the estimates are higher in pelagic fish such as tuna (*Thunnus thynnus*) and mackerel (*Scomber scombrus*). These species contain more fat than other fish like, e.g., the seabass, but the concentration increase can be due also to other factors like the size [21] and the relative food web position of the organism. The number of total PCB estimates in fish livers reported in scientific literature is low but in the fish previously considered, where reported, the concentration range result to be 166-5490 [20, 22] ng/g ww, while in the respective muscle (or total body) samples the range is 0.4-2200 [12, 18]. As already mentioned in previous studies on mammals [23] a hepatic sequestration of the contaminants of concern appears to exist.

Conclusions

In relation to both the number of ecotoxicological observations and the number of body burden estimations in target and non-target tissues, it was

possible to consider a preliminary risk assessment only for fish and mammals and for chemicals with a dioxin-like toxic action [24]. Other chemical families of potential toxicological concern (such as polychlorinated terphenyls (PCTs), polychlorinated naphthalenes (PCNs), polybrominated dibenzodioxins (PBDDs), etc.) appear to have been insufficiently characterized as to both the toxicological aspects and body burden estimates. Therefore determinations of these contaminants in environmental matrices should be a priority [3]. However, more work is necessary to define the role of these xenobiotics and their influence on natural communities.

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