Polychlorinated Biphenyls and Pesticides in Surficial Coastal Sediments of the Ligurian Sea

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Introduction

Polychlorinated biphenyls (PCBs) and chlorinated pesticides, such as DDT and its analogues, are organic contaminants widespread throughout the terrestrial and oceanic environments due to their common use and their resistance to degradation. Since harmful effects have been associated to these chemicals and well documented, they are classified as priority pollutants by both the US Environmental Protection Agency (EPA) and the European Union. Because of the very low solubility in water and the tendency to adsorb onto sediment particles, the ultimate fate of both PCBs and DDTs in the marine environment is the incorporation into sediments. Hence, the concentrations of these chlorinate chemicals in bottom sediments can provide an insight on the quality of the environment and the potential threat to marine organisms and human beings.

The Ligurian Sea belongs to the north part of the western Mediterranean. The coastal morphology of the Liguria Region is rather variable, and frequently cliffs drop sheer to the sea. The limited width of the coastal zone, comprised between the sea and the mountains, determined a gathering of the urban areas with a consequent concentration of both civil and industrial presence in a narrow but highly populated territory. In particular Genova, but also other cities have a long history of industrial and harbour activities, whereas long tracts of the coast are dedicated to tourism. The circulation of the Ligurian Sea is rather well known. In particular, surface and intermediate currents follow a cyclonic circulation. However local circulation is the true responsible of the dispersion of sediment material along the coast, and these alongshore currents often cause an eastward oriented transport.

The Ligurian coastal zone is very developed, and hosts all sort of industrial, agricultural and tourist activities that can be sources of persistent organochlorine chemicals. Therefore, the purpose of this study was to assess concentrations, distributions, sources and potential toxicological significance of PCBs and chlorinated pesticides in surficial sediments of the marine coastal area of the Ligurian Sea.

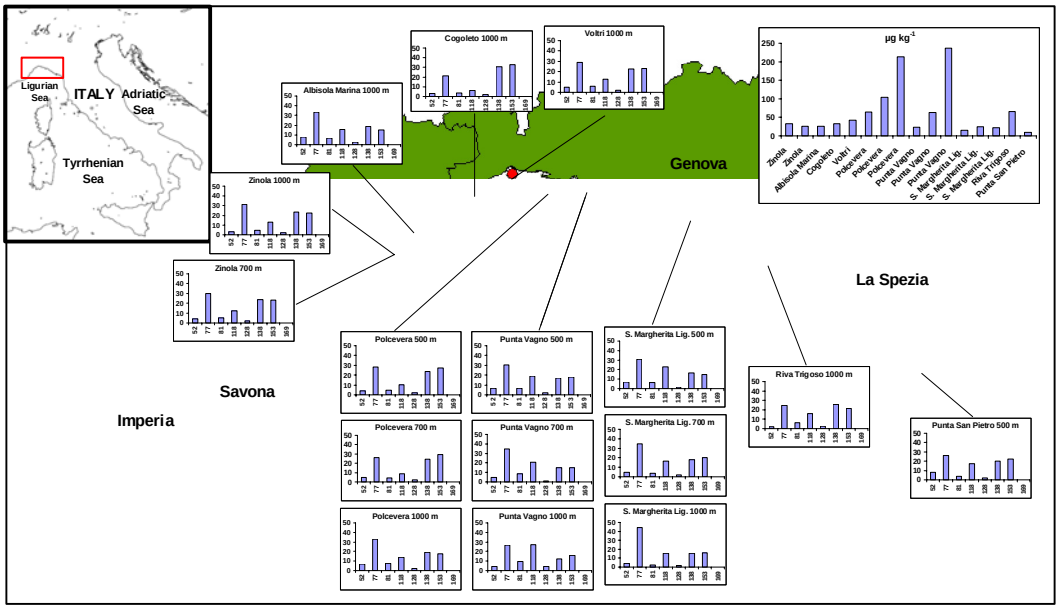
Materials and Methods

Sampling was carried out in 1999 at 75 stations in correspondence of the 25 localities shown in Figs. 1 and 2. Three samples were collected along each transect at 500, 700 and 1000 m from the shoreline, respectively. A Van Veen grab was used, whose penetration was typically 10-20 cm. We selected for the analysis only the topmost sediment (3 cm) that was carefully removed with a stainless steel spoon and transferred to glass screw cap jars with aluminium foil lid liners. The sediment samples were stored at -18°C before analysis.

We determined polychlorinated biphenyls (PCBs) and chlorinated pesticides. Among the latter, DDT and its analogues (4,4'-DDT, 2,4'-DDT, 4,4'-DDE, 2,4'-DDE, 4,4'-DDD, 2,4'-DDD), hexachloro cyclohexanes (α-HCH, β-HCH, γ-HCH, δ-HCH), aldrin, dieldrin, hexachlorobenzene, endrin, heptachlor plus heptachlor epoxide, endosulfan and metoxichlor.

Samples were dried 70-80°C overnight and then homogenized. Ten grams of dry sediment were extracted three times in ultrasonic bath for 15 min.: once with 50 ml of methylene chloride/isooctane/acetone (50:100:10, v/v), and twice with 50 ml of methilene chloride. The extracts, put together, were filtered with anhydrous Na_2SO_4 washing the residues two times with acetone/methylene (1:1, v/v), evaporated to dryness and redissolved with 3 ml of isooctane. Sulphur was removed by treating the solution several times with 0.5 ml of Hg, and non-persistent organic residues were eliminated using concentrated sulphuric acid. The determinations were carried out by HRGC-ECD. The identification of the single pesticides was based on retention times on at least three gas chromatographic columns of different polarities. The quantification was based on both external calibration (i.e. by comparison with the standards of the analysed pesticides), and the addition of an internal standard.

Figure 1: **Study area, sampling locations and PCB concentrations. The four provinces of the Liguria Region are indicated. One histogram shows PCB total concentrations and the others the congener relative abundances.**



PCB analyses were carried out by gas chromatography following the essentially the same described above for chlorinated pesticides. We quantified fourteen PCB congeners: CB-28, -31, -52, -77, -81, -101, -105, -118, -128, -138, -153, -156, -169, and -180 using external or internal calibration with aldrin. The method is able to reveal ca. 0.1 µg kg^{-1} (measured for CB-28) or less, as in the case of more chlorinated congeners.

Uncertainties (1 σ) were 2.4-24 and 6.1-19 % for PCBs and DDTs, respectively, with the lowest values corresponding to the highest concentrations. Repeated intercalibration exercises for both PCBs and chlorinated pesticides resulted in an average z score lower than ±2. All concentrations were calculated on a dry weight basis. The water content was measured by drying a known amount of sediment at 105°C until constant weight (usually overnight). Grain size analyses were carried out at the University of Genoa using sieves to separate the fines (silt pus clay) from the coarser sediment.

Results and Discussion

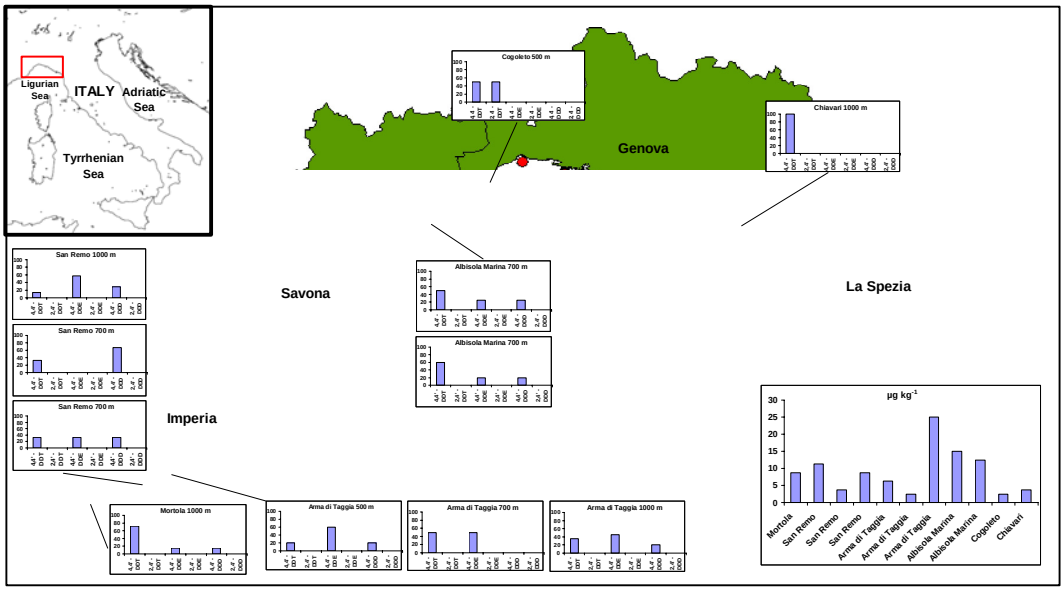
Sediment features: According to Bertolotto et al.[1], the hydrodynamics of the area drives sediment grain size in such a way that the content of fine particles (silt plus clay) increases going offshore: average values are 15.70 % at 500 m, 31.90 % at 700 m, and 46.34 % at 1000 m. The maximum contents of fines characterise sediments from the transect of Punta S. Pietro at 500 and 1000 m offshore (98.31 and 96.11 %, respectively). Silt is always prevalent with respect to clay that never

exceeds 9.16 %. Furthermore, the contents of fine particles and OC in sediments is strictly correlated.

Total concentrations: PCB concentrations are reported in Fig. 1, which also shows the relative importance of the seven congeners (CB-52, -77, -81, -118, -128, 138, -153) that could be find at 16 sites out of 75. The others (CB-28, -31, -101, -105, -156, -169 and -180) were always lower than detection limits (0.1 μg kg^{-1}), such as all PCBs at most places. When significant, PCB concentrations vary from 9.6 to 227 μg kg^{-1} and the maxima can be find in correspondence of very industrialised areas. Along a transect, usually the most contaminated sample is that 1000 m offshore, where the sediment is finer. Genova Punta Vagno (22.8-227 μg kg^{-1}) and Polcevera (62.4-206 μg kg^{-1}) are the most contaminated locations, followed by Riva Trigoso (62.8 μg kg^{-1}).
Concentrations of DDT and related compounds are reported in Fig. 2, whereas the values of the other eleven chlorinated pesticides are always below the limits of detection (ca. 1 μg kg^{-1}). Total DDT concentrations span the interval 2.5-25 μg kg^{-1}, with the highest values at Arma di Taggia (1000 m offshore), Albisola Marina (1000 m) and Sanremo (500 m).
It is useful to contrast our results with literature data from other places, although the comparison cannot be straightforward for PCBs because different authors either analysed different series of congeners or expressed the concentration with respect to Aroclor standard mixtures. The highest PCB concentrations in our samples appear lower than maximum values reported for polluted localities in Australia (0.5-790 μg kg^{-1}), China (11.5-485 μg kg^{-1}), India (4.8-1000 μg kg^{-1}), Scotland (0.5-500 μg kg^{-1}), Thailand (11-520 μg kg^{-1}), and Vietnam (0.2-630 μg kg^{-1}) by Fillmann et al.[2] and references therein. In turn, the same authors reported values of 5.9-220 μg kg^{-1} (Indonesia), 63-240 μg kg^{-1} (Japan), and 2.3-230 μg kg^{-1} (Taiwan) that are of the same order of magnitude than ours. As far as the north-western Mediterranean is concerned, literature were summarised by Picer[3], who reported an interval of concentrations 0.2-15850 μg kg^{-1}. Regarding DDTs, the values 0-20 μg kg^{-1} are relatively low in comparison with those listed by Fillman et al.[2]: 0.08-1700 μg kg^{-1} (Australia), <0.1-1027 μg kg^{-1} (South Pacific Islands), 0.4-790 μg kg^{-1} (Vietnam), 9.3-750 μg kg^{-1} (Solomon Island). According to Picer[3] , values in the interval 0.4-200 μg kg^{-1} have been found in the north-western Mediterranean.

Obviously, the general trends of both PCBs and DDTs suggest that concentrations can be a function of grain size and OC contents only at a transect scale, whereas the significant presence of these contaminants is clearly a function of the relative importance of point sources.

Figure 2: **Distribution and relative importance of 4,4'-DDT, 2,4'-DDT and their metabolites. Total concentrations are also reported.**

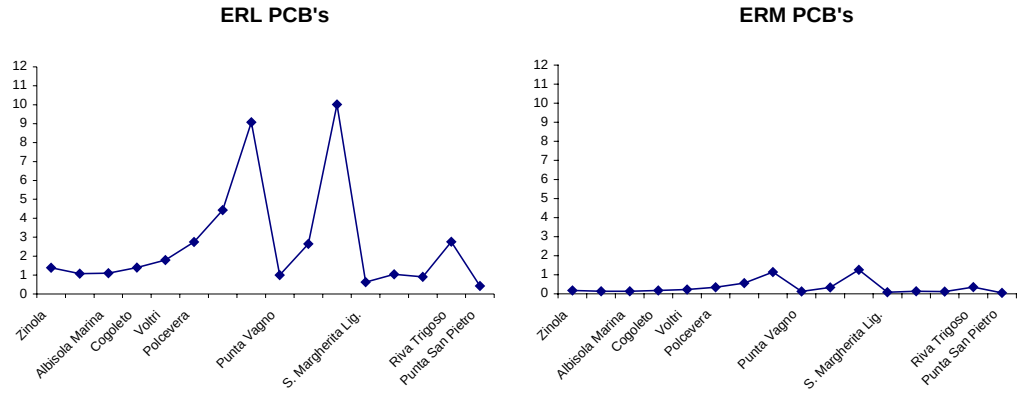


Source identification: The highest PCB concentrations correspond to transects located in front of the urban centre of Genova. In particular the Bisagno Torrent, which crosses a densely populated and industrialised area, flows very close to Punta Vagno. Here the passage of ferries, holiday cruisers and container ships going to the Port of Genova is very frequent. Not far is located a coal power plant, and Punta Vagno hosts one of the most important treatment plants of the city (300.000 Equivalent Inhabitants). On the other hand, the transect of Polcevera is located in front of the homonymous torrent, which drains an area of maximum industrial concentration with steelworks, refineries, other minor enterprises with a high pollution potential and a treatment plant (125.000 Equivalent Inhabitants). Not far is located the oil terminal of Genova Multedo, where the big tanks dock and the oil is treated to be exported to other countries. The area hosts four refineries and plants for mixing and treatment of oil products. Furthermore, the transect of Riva Trigoso is placed in front of an area characterised by an important shipyard.

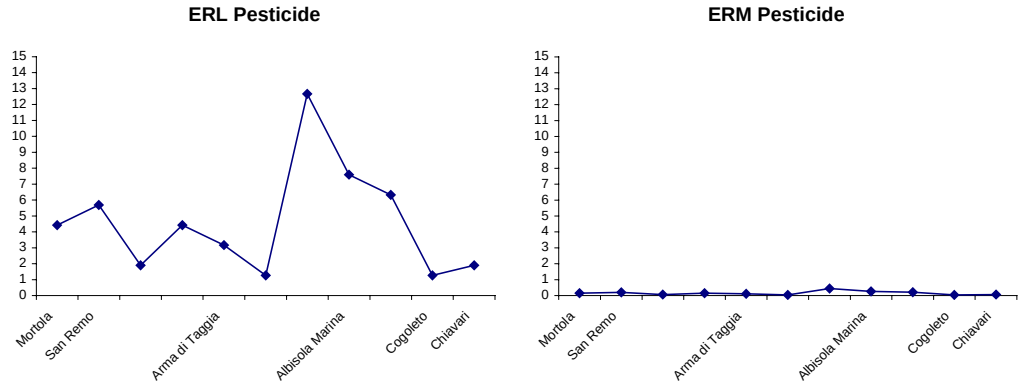
As expected, because of the difference in the sources, the contamination of DDTs is significant at locations others than those influenced by PCBs. Relatively high values were found at Arma di Taggia and Albisola Marina, followed in the order by Sanremo, Mortola, Chiavari and Cogoleto. This distribution can be explained on the basis of what is known about the use of pesticides in agriculture: actually, the area next to Sanremo and Arma di Taggia transects hosts several greenhouses and floricultural activities.

Figure 3: Distribution of ERL and ERM quotients (a: PCBs; b: total DDT). Samples along the same transect are listed from 500 to 1000 m offshore, in the order.

a)



b)



Congener proportions: It is known that factors such as differential water solubility, preferential accumulation and biodegradation of different congeners can change the original proportions of PCBs and DDTs. Figs. 1 and 2 shows that there are different profiles, which means that the relative abundance of both PCB and DDT congeners changes due to either a different contribution of the source or selective processes such as volatilisation, adsorption, transport and diagenesis. The relative proportions of PCBs show different profiles. These can be affected to some extent by the low resolution of the analytical method. However, some comments are possible. Picer[3], discussing DDTs and PCBs in the Adriatic sea, reported data from seven sectors of the Mediterranean: major components of technical PCB mixtures (CB-28, -110, -118, -138, -153 and -180) are almost always found as the most important congeners in abiotic samples.

However, this is not strictly valid in our case because, of this list, only CB-118, -138 and -153 were found. CB-77 is almost always the most abundant, followed by CB-138 and -153 which, in turn, clearly prevail at Cogoleto. In a few cases, CB-118 assumes a higher relative importance than CB-138 and -153, whereas in one case is the most abundant. The contribution of CB-52, -81 and -128 is always low, and CB-169 was never found.
DDT compositional ratios (4,4'-DDE/4,4'-DDT), when calculable, range between 0.2 to 4 (average 1.02) with most values spanning the interval 1-4. These variations in compositional ratios are common[3] and depend on DDT degradation. High values suggest that much time has elapsed since the usage of the pesticide. This seems to be our case, except for the sample taken from Chiavari, where 4,4'-DDT is the only congener and no metabolites are present.

Potential toxicological significance: ERL and ERM quotients[4,5] were calculated for each sample by dividing total PCB concentrations by 22.7 and 180 μg kg^{-1}, respectively. ERL and ERM quotients were also calculated for DDTs using the values 1.58 and 46.1 μg kg^{-1}. Fig. 3 shows the results.
Among the 16 samples with significant PCB concentrations, thirteen have a mean ERL quotient higher than 1. This means that adverse biological effects are likely to occur only occasionally for the most sensible species[5] but are more probable at Polcevera and Punta Vagno, 1000 m offshore, where also the ERM guidelines are exceeded.
Regarding DDTs, all samples with significant values exceed the ERL guidelines, whereas none of them has ERM quotients higher than 1. This means that, as far as DDTs are concerned, adverse effects can develop but only occasionally[4,5].

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