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Polychlorinated biphenyls (PCBs) in sediments from the western Adriatic Sea: Sources, historical trends and inventories

Tatiane Combi [a,*], Stefano Miserocchi [b], Leonardo Langone [b], Roberta Guerra [a,c]

[a] Centro Interdipartimentale di Ricerca per le Scienze Ambientali (C.I.R.S.A.), University of Bologna, Campus di Ravenna, Ravenna 48123, Italy
[b] National Research Council of Italy, Institute of Marine Sciences (CNR-ISMAR), Via Gobetti 101, 40129 Bologna, Italy
[c] Department of Physics and Astronomy, University of Bologna, Bologna, Italy

[*] Corresponding author: tatiane.combi4@unibo.it

Abstract

Sources, historical trends and inventories of polychlorinated biphenyls (PCBs) were investigated in sediments collected in five transects along the north-south axis of the western Adriatic Sea. The concentration of total PCBs (Σ_{28} PCBs) ranged from bLOD (limit of detection) to 9.0 ng g^{-1} in the sediment cores and between 0.1 and 2.2 ng g^{-1} in recent sediments. Chronological records of PCB concentrations displayed a common pattern with historical PCB production and use, with the maximum peak values detected between the 1960s and the 1980s. Sediments deposited within the last two decades presented a ~40% to ~80% PCB reduction in comparison to the peak levels, reflecting the ban on PCB production and use since the late 1970s. PCB levels along with the presence of high-chlorinated congeners decreased southwards, indicating the Po River as the major source of PCBs in the western Adriatic Sea. This is further corroborated by the estimated inventories of PCBs, which were ~4–7 times higher in the Po River prodelta (256 ng cm^{-2}) in comparison to the middle and southern Adriatic, respectively, and about 100 times higher than the in the deep Adriatic Sea.

Keywords Persistent organic pollutants, Sediment cores, Homologue patterns, Fluxes, Adriatic mud-wedge

1. Introduction

Polychlorinated biphenyls (PCBs) are a classical group of persistent organic pollutants (POPs) that were extensively used worldwide since they were first produced, in 1930. Due to their physical-chemical properties, PCBs were mainly used as electric fluids in transformers and capacitors, hydraulic lubricants and flame retardants, and to a lesser extent, in plasticizers, carbonless copy paper, paints, among numerous other applications (Fiedler, 1997; Borja et al., 2005). Global production of PCBs was estimated to exceeded 1.3 million tons and Italy is among the major consuming countries corresponding to over 2% of global PCB consumption (Breivik et al., 2007). PCB production and usage have been globally restricted since the 1970s because of their adverse effects, including endocrine disrupting and carcinogenic effects and biomagnification properties (Borgå et al., 2001; Frignani et al., 2007).

In spite of the production and use ban, PCBs are still in use in closed systems, especially in electrical equipment. Consequently, PCBs can still be detected in the environment, and their current levels are not expected to decrease significantly within the next few decades (Breivik et al., 2007; Sobek et al., 2015). Currently, PCBs can reach the environment by urban and industrial sewage discharge, leaching from contaminated soils, direct spillages into soils, urban runoff and volatilization (Breivik et al., 2002b; Litskas et al., 2012). PCBs are mainly transported from sources by atmosphere and water bodies to the open sea, where sediments usually represent their final sink (Ruiz-Fernández et al., 2012; Argiriadis et al., 2014).

The Adriatic Sea is a shallow semi-enclosed basin connected to the Mediterranean Sea through the Strait of Otranto (Manca et al., 2002). Human activities and their influences are intensive in the area pressuring the Adriatic marine ecosystems. Consequently, the Adriatic Sea is an important and interesting area for pollution studies sheltering heavily industrialized, urbanized and agriculturally productive areas (Dujmov et al., 1993). The major sources of POPs have been related to coastal industrial activities as well as riverine discharges, especially associated with the Po River, which is the largest and most important Italian river (Galassi and Provini, 1981; Guzzella and De Paolis, 1994; De Lazzari et al., 2004). In the Adriatic Sea, the dispersion of riverborne materials and associated pollutants is driven by the general cyclonic water circulation and oceanographic conditions. Consequently, fine sediments accumulate in a belt parallel to the Italian coast (Correggiari et al., 2001; Frignani et al., 2005).

There is little data related to the occurrence and levels of PCBs in sediments from the Adriatic Sea, which has been observed since the 1990s (Fowler et al., 2000; De Lazzari et al., 2004; Pozo et al., 2009). Although there is plenty of information regarding contaminant concentrations in coastal and riverine systems in the Adriatic Sea (Galassi and Provini, 1981; Acquavita et al., 2014; Guerra et al., 2014; Viganò et al., 2015), marine sediments have been studied to a lesser extension and usually within delimited regions (e.g. Caricchia et al., 1993; Fowler et al., 2000). A wide-ranging work is fundamental for a comprehensive understanding of the extension and patterns of PCBs at the Adriatic Sea basin level, providing tools to identify the evolution of anthropic pressures and possible threats to the Adriatic ecosystem as a whole.

The aim of this work is to assess historical patterns, inventories and potential sources of PCB in sediments along the western Adriatic Sea. This work is part of the PERSEUS EU FP7 Project (Policy-oriented Marine Environmental Research in the Southern European Seas), which aims to provide information on pressures and impacts considered as major threats to the good environmental status of the marine systems, addressing them to the Marine Strategy Framework Directive (MSFD) descriptors.

2. Material and methods

2.1. Sampling

Sediments were collected on the mud-wedge along five transversal-to-the-coast transects placed from northern to southern Adriatic Sea on board the R/V Urania in April 2013 (southern Adriatic), R/V Dallaporta in November 2013 (central and southern Adriatic) and R/V Urania on February 2014 (northern Adriatic). Undisturbed sediment cores (one key-station for each transect) were retrieved in the Po River prodelta (core J25), Ancona (core AN2), the Gargano Promontory (core GG2), Bari (core BA5) and the Gondola slide (core DE15bis) (Fig. 1).

Sediment cores (length ≤ 50 cm; diameter: 10 cm) were collected using a cylindrical box-corer or the gravity sediment corer SW104, specially designed to preserve the sediment-water interface, and sectioned onboard at 1-cm intervals. Surface sediments were taken by a mini box corer or oceanic box corer and the top 0.5 cm of undisturbed sediment was collected. All samples were placed into pre-cleaned glass jars with aluminum foil liners on the lid to avoid potential leaching, and stored at −20 °C until processing and analysis.

2.2. Sediment characteristics and estimated date

In the laboratory, all sediment layers were weighed, oven-dried at 55 °C, and then re-weighed to determine water content. Porosity (ϕ) was calculated from the loss of water between wet and dry sediments according to equations suggested by Berner (1971), assuming a sediment density of 2.6 g cm^{-3} and a water density of 1.034 g cm^{-3}. Grain size was determined after a pre-treatment with H_2O_2 and wet sieving at 63 μm to separate sands from silt and clay fractions. Total and organic carbon (OC) and total nitrogen (TN) content were measured on a Fison CHNS-O Analyzer EA 1108. Samples for OC analysis were first decarbonated after acid treatment (1.5 M HCl). Based on the analysis of replicate samples, the average standard deviation (SD) of the results was ±0.07 and ±0.01% for OC and TN, respectively (Tesi et al., 2007).

Sediment accumulation rates (SARs) and mass accumulation rates (MARs) based on radioisotope geochronology (mainly ^{210}Pb and ^{137}Cs) were extensively assessed in the Adriatic Sea. Accordingly, different datasets were combined based on triangle-based linear interpolation in order to obtain better spatial distribution (Frignani et al., 2005; Palinkas and Nittrouer, 2007; Tesi et al., 2013). Since information on accumulation rates and strata chronologies in the deep Adriatic is scarce, sediment core sampled in the Gondola site (core DE15bis) was measured for ^{210}Pb activities. Alpha counting of daughter isotope ^{210}Po, considered in secular equilibrium with its grandparent Ra^{226}, was used for ^{210}Pb analyses. Estimated SAR for each key-station is reported in Table 1. The highest SARs were observed in the Po River prodelta (0.79 ± 0.12 cm y^{-1}) where sediments accumulate preferentially in two depocenters (Tesi et al., 2013). Other important sites of deposition are Ancona (AN2; 0.35 ± 0.04 cm y^{-1}) and the Gargano promontory (GG2; 0.46 ± 0.06 cm y^{-1}).

In order to estimate the date for each section of the sediment cores, the sediment accumulation rate reported for each key-station was used, as follows:

$$\text{Estimated date } [\textit{anno Domini}(\text{A.D.})] = a - \left(\frac{b}{c}\right)$$

where a is the year in which the core was collected, b is the depth of the section in the core and c is the SAR of each core (Martins et al., 2014).

2.3. PCB analyses

Whole sediment samples were air-dried under a fume hood and then homogenized using a blender. Approximately 10 g of dried sediments were placed in pre-cleaned cellulose thimbles and TCMX (tetrachloro-*m*-xylene, AccuStandard, USA) was added as surrogate standard. Samples were Sohxlet extracted using a mixture of acetone and *n*-hexane (20:80) for 16 h. Clean-up and fractionation of the extracts was accomplished through passage on an acidic silica gel column (30% H_2SO_4) and activated copper powder was used to eliminate interfering sulphur compounds (adapted from US EPA, 2008). PCBs were eluted with 60 mL of a dichloromethane (DCM) and

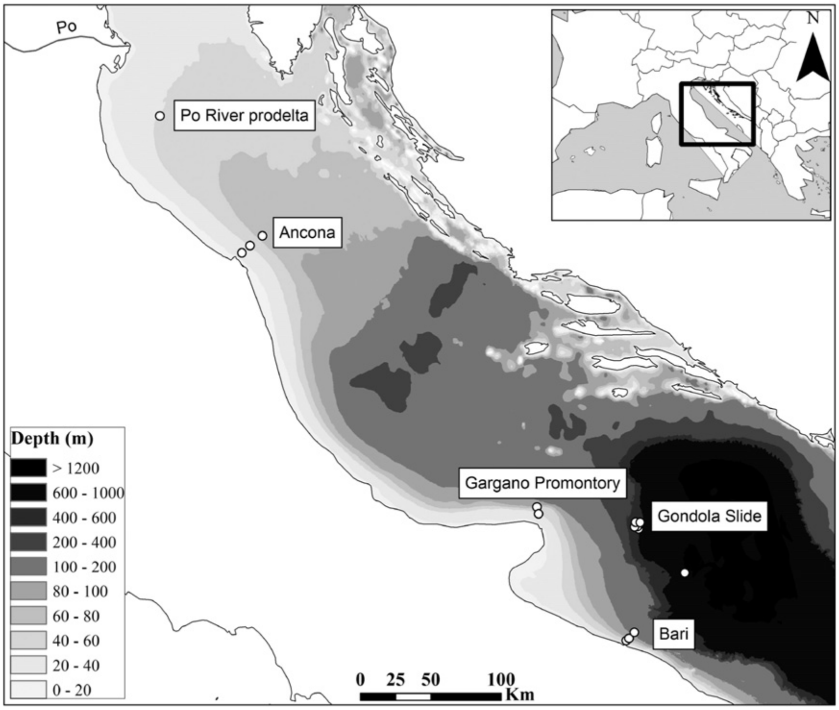

Fig. 1. Map of the Adriatic Sea indicating sediment sampling stations: the Po River prodelta, Ancona, the Gargano Promontory, Bari and the Gondola slide.

n-hexane mixture (40:60). The extracts were concentrated to a final volume of 1 mL under a gentle gas stream of purified nitrogen. PCB 198 (AccuStandard, USA) was added to the samples prior to the injection as internal standard.

The determination of PCBs was performed by gas chromatography (GC Varian CP 3800) with electron capture detection (ECD) equipped with a Supelco MDN-5S column (length: 30 m, ID: 0.25 mm, film thickness: 0.25 μm). The oven temperature started with 100 °C for 2 min, increasing of 15 °C per minute until 160 °C and increasing 5 °C until 270 °C with a final hold time of 10 min. The equipment calibration was made with a calibration curve prepared with a PCB standard (C-WNN, AccuStandard, USA, 28 congeners: PCB 8, PCB 18, PCB 28, PCB 52, PCB 44, PCB 66, PCB 101, PCB 81, PCB 77, PCB 123, PCB 118, PCB 114, PCB 153, PCB 105, PCB 138, PCB 126, PCB 187, PCB 128, PCB 167, PCB 156, PCB 157, PCB 180, PCB 169, PCB 170, PCB 189, PCB 195, PCB 206, PCB 209) at the following concentrations: 1, 2, 5, 10 and 20 ng mL^{-1}. The analytes were identified by comparison of the retention times of the peaks detected in each replicate with the peaks obtained on the calibration curves. The quantification of the PCBs was based on the area obtained for each analyte in the samples, according to the mass/area ratio obtained for the internal standard and on the response factor obtained from the calibration curve. Confirmatory analysis of selected PCB peaks was accomplished by GC/MS analysis (Agilent HP 5970 MSD interfaced to an HP 5890 GC). Concentrations of single PCB congeners and $\sum_{28}$ PCBs are given in ng g^{-1} sediment dry weight.

2.4. Quality-assurance procedures

The quality-assurance procedures included precision tests, analyses of procedural blanks and matrix spikes (Wade and Cantillo, 1994). The mean surrogate recovery, based on the relationship with the internal standard (PCB 198) added before the GC-ECD analyses, was of 90.0 ± 13.8%. Spike tests were performed by analyzing a replicate sediment from a reference site spiked with the PCB standard. The mean standard recovery in the spike tests was 94.0 ± 12.7%, with mean relative standard deviation (RSD) of 12.4 ± 5.1%. A procedural blank was performed for each extraction batch using 10 g of anhydrous sodium sulfate heated to 450 °C prior to extraction and analyzed in the same way as the samples. The limit of detection (LOD) was calculated as the average blank value plus three times the standard deviation of the blanks, and varied between 0.01 and 0.26 ng g^{-1} (Table S1).

Table 1
Location, depth, sediment characteristics and PCB inventories in sediment cores from the western Adriatic Sea: organic carbon (% OC), C/N atomic ratio, fine sediments (% mud), estimated SARs (g cm^{-2}), and PCB inventories (ng cm^{-2}). Minimum, maximum, mean and standard deviation (SD). Mud: silt and clay.

	Po river prodelta	Ancona	Gargano Promontory	Bari	Gondola slide
	J25	AN2	GG2	BA5	DE15bis
Latitude (N)	44°83.42′	43°42.414′	41°59.265′	41°10.611′	41°54.347′
Longitude (E)	12°58.98′	13°38.443′	16°09.066′	16°53.729′	16°58.206′
Depth (m)	26	42	34	74	522
OC	1.08–1.28 (1.2 ± 0.04)	0.58–0.83 (0.7 ± 0.05)	0.40–0.70 (0.6 ± 0.04)	0.6–0.94 (0.8 ± 0.06)	0.43–0.65 (0.5 ± 0.06)
C/N	9.7–11.7 (11 ± 0.4)	9.1–10.5 (10 ± 0.2)	7.1–10.7 (9.7 ± 0.4)	8.7–10.7 (9.5 ± 0.3)	7.1–9.6 (8.4 ± 0.7)
Mud	99.1 ± 0.35	99.2 ± 0.2	96.8 ± 0.9	97 ± 1.2	91.2 ± 1.6
Estimated SARs	0.79 ± 0.12	0.35 ± 0.04	0.46 ± 0.06	0.30 ± 0.02	0.08 ± 0.006
PCB inventories	256	63	35	37	2.5

Table 2
Depth and sediment characteristics of the surface sediments from the western Adriatic Sea: mean PCB concentration (ng g^{-1}), organic carbon (% OC), C/N atomic ratio, fine sediments (% mud). Mud: silt and clay.

		Depth (m)	PCB	OC	C/N	Mud
Ancona	AN1	20	1.4 ± 0.6	0.59	8.8	94.0
	AN2	40		0.81	9.4	99.3
	AN3	65		0.91	9.2	97.6
Gargano Promontory	GG1	70	–	0.63	9.9	93.0
Bari	BA4	55	1.2 ± 0.3	0.82	9.2	94.0
	BA5	78		0.83	9.4	93.8
	BA6	110		0.76	8.9	96.7
Gondola slide	DE 01	1060	0.2 ± 0.1	0.66	8.3	88.8
	DE 06	580		0.66	8.4	94.0
	DE 09	560		0.68	8.7	92.2
	DE 19	520		–	–	73.3
	DE 21	580		–	–	96.2

3. Results and discussion

3.1. Sediment characteristics

Summary results regarding grain size distribution, OC and OC/TN atomic ratio are presented in Table 1 for sediment cores and Table 2 for surface sediments. Fine fractions (silt and clay) were predominant in sampled sediments accounting for 73.3–99.8%. Grain size data are comparatively uniform and consistent with other studies accomplished within the western Adriatic mud-wedge (Frignani et al., 2005; Cattaneo et al., 2007; Tesi et al., 2007, 2013 and references therein; Romano et al., 2013), where the sediment released to by the Po and Apennine rivers consists primarily of (>90%) silt and clay particles (i.e., smaller than 64 μm) (Nittrouer et al., 2004). OC exhibited a relatively low content and a limited variability in the mud-wedge sediments from the Adriatic Sea, varying between 0.4 and 1.3% (0.7 ± 0.1%).

These levels are consistent with previous data on OC content found in sediments from the western Adriatic Sea (Tesi et al., 2007; Turchetto et al., 2007; Tesi et al., 2013). In general, OC and C/N ratio presented a decreasing trend from northern to southern Adriatic Sea, with mean OC values of 1.2 ± 0.04 and 0.5 ± 0.06% and mean C/N ratios of 11 ± 0.4 and 8.4 ± 0.7 from the Po River prodelta (core J25) to the Gondola slide (core DE15bis), respectively. No correlations were detected between grain size and OC and PCB concentrations.

3.2. PCB levels and trends

Individual and total PCB concentrations (ng g^{-1}) in surface samples and sediment cores are available in the Supplementary material (Tables S1–S6). The concentration of total PCBs ($\sum_{28}$ PCBs) ranged between 0.1 and 2.2 ng g^{-1} in surface sediments from Ancona (AN1, AN2, AN3), the Gargano promontory (GG1, GG2), Bari (BA4, BA5, BA6), and the Gondola slide (from DE1 to DE21), and from <LOD to 9.0 ng g^{-1} in the sediment cores (J25, AN2, GG2, BA5, and DE15bis). In general, $\sum_{28}$ PCB concentrations in surface samples decreased seaward with water depth, with the maximum concentration detected much closer to the coast in Ancona (AN1, 2.2 ng g^{-1}). The concentrations found between the 60 m and 80 m isobaths (sediments AN3, BA4, BA5 and GG1) were very similar, with a mean concentration of 1.4 ± 0.2 ng g^{-1}.

$\sum_{28}$ PCB concentrations also decreased southwards. The highest concentrations were detected in the sediment core close to the Po River prodelta (J25) in the top 1-cm layer and at 20 cm depth (5.2 and 9.0 ng g^{-1}, respectively). In the southern Adriatic (represented by key-stations in the Gargano Promontory and Bari), $\sum_{28}$ PCB concentrations ranged from 0.3 to 2.2 and from <LOD to 3.2 ng g^{-1} (cores GG2 and BA5, respectively). The lowest concentrations were detected around the mud wave field located on the north of the Gondola slide (DE01 to DE21), where total PCB concentrations ranged from 0.1 to 0.3 ng g^{-1} for surface sediments and from <LOD to 1.4 ng g^{-1} for the sediment core DE15bis.

Table 3
PCB ranges (ng g^{-1}, expressed at the minimum and maximum values) founded in sediments from different marine areas worldwide.

Location	PCBs (ng g^{-1})	References
Adriatic Sea	<LOD–9.0	This work
Northern Adriatic Sea	3–80	Caricchia et al. (1993)
Northern and Middle Adriatic	0.9–14.7	Fowler et al. (2000) and De Lazzari et al. (2004)
Western Adriatic Sea coastal areas	0.3–84	Pozo et al. (2009)
Eastern Adriatic Sea	<0.5–294	Picer and Picer (1991)
Mar Piccolo, Southern Italy	2–1684	Cardellicchio et al. (2007)
Crete, Eastern Mediterranean Sea	0.038–1.2	Mandalakis et al. (2014)
Catalonia and Andalusia coastal areas, Mediterranean Sea, Spain	0.1–15.1	Eljarrat et al. (2005) and Solé et al. (2013)
Baltic Sea	0.71–74	Sobek et al. (2015)
Barents Sea	<LOD–3.5	Zaborska et al. (2011)
Caribbean Sea	<LOD–441.6	Fernandez et al. (2007) and references therein
Salton Sea, USA	116–304	Sapozhnikova et al. (2004)
Yangtze River Estuary and East China Sea	5.08–19.64	Yang et al. (2012)

The concentrations detected in recent surface sediments in this study present a significant decrease in comparison to those previously detected in northern and middle Adriatic (Caricchia et al., 1993; Fowler et al., 2000) and in the eastern Adriatic (Picer and Picer, 1991), reflecting the restrictions on use and productions of these compounds (Table 3). In general, total PCB concentrations detected in the southern Adriatic were similar to those obtained for deep sediments of the eastern Mediterranean Sea (Mandalakis et al., 2014) and in coastal areas from Spain (Eljarrat et al., 2005; Solé et al., 2013. Total PCB concentrations in the sediment core collected close to the Po River prodelta (J25) were similar to those previously reported in the northern Adriatic (Fowler et al., 2000; De Lazzari et al., 2004), but lower than those registered in more industrialized and urbanized areas, such as the Mar Piccolo of Taranto (Cardellicchio et al., 2007), the East China Sea (Yang et al., 2012), the Baltic Sea (Sobek et al., 2015), and the Salton Sea (Sapozhnikova et al., 2004).

Gómez-Gutiérrez et al. (2007) proposed background levels of contamination for the Mediterranean Sea. With reference to PCB contaminants, these levels were established as 1–5 ng g^{-1} (median 2 ng g^{-1}) as the sum of seven indicator PCB congeners ($\sum_7$ PCBs: PCBs 28, 52, 101, 118, 138, 153, and 180). $\sum_7$ PCB levels were above the background levels only in the Po River prodelta (sediment core J25), where 70% of the sediment samples exceeded the median background level, and the $\sum_7$ PCB concentrations ranged from 1.0 to 5.5 ng g^{-1}. Concerning the environmental quality standards (EQS), the Italian Decree n. 260/2010 (D.M. 260/2010) set an EQS of 8 ng g^{-1} for PCB in sediments of transitional and coastal environments ($\sum_{13}$ PCB 28, 52, 77, 81, 101, 118, 126, 128, 138, 153, 156, 169, 180). The $\sum_{13}$ PCB levels detected in this work did not exceed, in any sediment core, the proposed EQS. 0.09pt?>Further studies considering additional parameters (e.g. other classes of contaminants) are warranted to the estimation and evaluation of possible ecotoxicological risks in sediments from the western Adriatic Sea.

3.3. PCB composition and sources

As the physico-chemical properties of PCBs are dependent on their degree of chlorination (Fiedler, 1997), the analysis of PCB congeners and homologue profiles provide useful insights on the behavior and the possible sources of PCBs to the marine environment (Mai et al., 2005; Barakat et al., 2013).

In general, dominant PCB congeners were PCB 81, PCB 8, PCB 209, PCB 187 and PCB 118 (Tables S1–S6 from Supplementary material). While congener composition was considerably different among the sediment cores, surface samples displayed an analogous predominance of low-chlorinated congeners (especially PCB 8 and PCB 81). This pattern indicates the same origin of PCBs and low influence of local input sources in recent sediments (Tolosa et al., 1995; Barakat et al., 2013). Low-chlorinated PCBs are more volatile and less persistent in the marine environment, being usually related to long-range transport and/or dechlorination processes, while the higher chlorinated compounds are associated to local input sources and contaminated areas (Tolosa et al., 1995; Borja et al., 2005).

Differences among areas in the western Adriatic Sea, tested by one-way ANOVA, were significant for PCB homologue composition (F-ratio $= 6.7$, p value < 0.05). The tetra-chlorinated biphenyls (tetra-CB) were the most prevalent homologues in sediment from Bari, the Gargano Promontory and the Gondola slide (cores BA5, GG2 and DE15bis), accounting for ~70%, 60% and 40% of the total PCBs, respectively. Conversely, penta- and hepta-chlorinated biphenyls were the dominant homologues in Ancona (core AN2) and Po River prodelta (core J25), representing ~40% and 30% of the total PCBs, respectively. Different homologue composition among sediment cores may be related to variable inputs of PCB mixtures to the western Adriatic Sea (Fowler et al., 2000).

Higher abundance of the low-chlorinated congeners (di-, tri-, tetra- and penta-CB) were detected in middle and southern Adriatic, with an average contribution ranging from ~60% to nearly 100% in sediment cores from Bari, the Gargano Promontory and the Gondola slide (BA5, GG2 and DE15bis) (Fig. 3). In general, the contribution of high-chlorinated congeners (hexa- to deca-CB) decreased southwards, from ~50% in the Po River prodelta (core J25) to ~2–3% in the Gargano Promontory (core GG2). The decreasing patterns of total and particularly higher-chlorinated PCBs from the northern to the southern Adriatic Sea and the prevalence of lower-chlorinated congeners in the southern cores suggest a predominant influence of the Po River discharge in the Northern Adriatic. The Po River has a drainage basin of 75,000 km^2 being one of the main drainage basins in Europe. It extends eastward across northern Italy and receives influences from highly urbanized and industrialized areas thus representing one of the major sources of PCBs and other contaminants to the Adriatic Sea (Guzzella and De Paolis, 1994; Tesi et al., 2007; Viganò et al., 2015).

Even though low-chlorinated congeners were predominant in southern Adriatic, the presence of some high-chlorinated PCBs found within the Gondola slide, especially hexa- and hepta-CB (PCB 138 and PCB 157), may indicate local input sources. Considering that these samples were taken from a remote, deep-sea area (500 to 600 m depth), the presence of PCB sources seems to be unlikely. A possible explanation for the presence of high-chlorinated congeners is the influence of the cascading of the North Adriatic Dense Water (NAdDW) in the area (Turchetto et al., 2007; Tesi et al., 2008), which in particular periods is able to quickly transfer suspended particles coming from the North Adriatic (Langone et al., 2016). The NAdDW is the densest water of the whole Mediterranean, formed over the Adriatic northern shelf during cold months and spreading southward along the western Italian shelf reaching the southern Adriatic basin (Vilibić and Supić, 2005). The intensity of the NAdDW cascading depends on numerous factors (e.g. atmospheric temperature; precipitation; bottom morphology), playing a first order control on the particulate fluxes through the western margin of the Southern Adriatic (Langone et al., 2016).

Although reductive dechlorination of PCBs can occur in anoxic environments, leading to transformation of PCB congener composition from higher to lower-chlorinated compounds over time (Zoumis et al., 2001; Borja et al., 2005; Sobek et al., 2015), downcore distribution of low- and high-chlorinated PCBs was rather constant within cores and no shift on homologue composition was evident; hence, dechlorination processes are not likely to occur in the sediments of the western Adriatic Sea (Fig. 1 of Supplementary material).

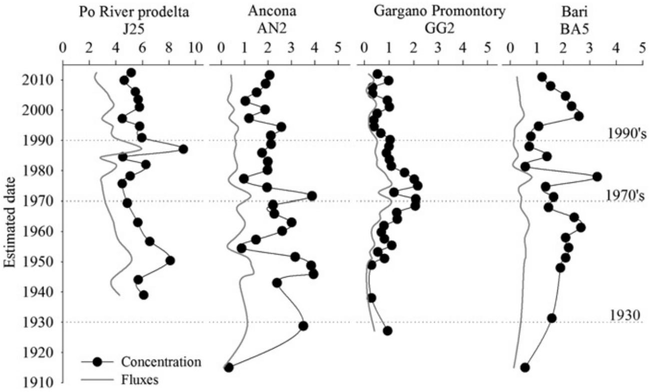

Fig. 2. Historical trends of PCB concentrations (ng g^{-1}) and fluxes (ng cm^{-2} y^{-1}) in sediment cores from the western Adriatic Sea.

3.4. Historical records of PCBs

Downcore variation of $\sum_{28}$ PCB concentrations (ng g^{-1}) in the sediments from the western Adriatic Sea is showed in Fig. 2. Annual PCB fluxes (ng cm^{-2} y^{-1}) were estimated as follows:

$$\mathrm{Flux} = C_i r \rho_i$$

where C_i is the concentration of $\sum_{28}$ PCBs in sediment layer i (ng g^{-1}), r is the SAR for each sediment core (cm y^{-1}) and ρ_i is the dry mass of the sediment layer i (g cm^{-3}; Mai et al., 2005).

Calculated PCB fluxes followed the same patterns as those detected for $\sum_{28}$ PCB concentrations (Fig. 2). Briefly, the bottom layers of the sediment cores (sediments deposited before 1940) registered the lower mean PCB fluxes, ranging from 0.01 ng cm^{-2} y^{-1} in Ancona (core AN2) to 4.3 ng cm^{-2} y^{-1} in the Po River prodelta (core J25). PCB fluxes were fairly low and constant until the middle of the 1960s, where mean values ranged from 0.3 ± 0.1 ng cm^{-2} y^{-1} offshore the Gargano Promontory (core GG2) to 4.2 ± 0.4 ng cm^{-2} y^{-1} in the Po prodelta (core J25). Maximum values of 4.7 ng cm^{-2} y^{-1}, 1.3 ng cm^{-2} y^{-1}, 1.1 ng cm^{-2} y^{-1} and 0.8 ng cm^{-2} y^{-1} were detected between the 1970s and the early 1990s in the Po River prodelta, Ancona, the Gargano Promontory and Bari, respectively. A subsequent decrease reaching back constant levels of ~2–3 ng cm^{-2} y^{-1} in the Po River prodelta (core J25), ~0.4 ng cm^{-2} y^{-1} in Ancona and Bari (cores AN2 and BA5), and ~0.3 in the Gargano Promontory (core GG2) occurred in the last two decades.

Historical trends of total PCB ($\sum_{28}$ PCBs) showed a common pattern, with increasing concentrations from the lower horizons to the middle sections of sediment cores from the Po River prodelta, Ancona, the Gargano Promontory and Bari followed by a decreasing trend upwards in the surface layers deposited in recent years (Fig. 2). Sediments from the Gondola slide (core DE15bis) present particular characteristics (e.g. distance from the coast and non-detectable or negligible PCB concentrations), that makes it unsuitable for the reconstruction of PCB historical record. Therefore, these data will not be discussed for PCB historical records hereafter.

Low concentrations of total PCBs ($\sum_{28}$ PCBs: 0.1–3.5 ng g^{-1}) were detected in sediments deposited prior to the period of first PCB production (before 1930). Similar observations for PCB concentrations were extensively reported in previous works (e.g. Mai et al., 2005; Frignani et al., 2007; Piazza et al., 2009; Mugnai et al., 2011) and were ascribed to a number of factors, such as physical mixing of sediments, bioturbation, and/or downward migration of PCB congeners in the sediment column. Similarly to the results reported by Mai et al. (2005), low-chlorinated PCBs were in general more abundant in sediments deposited before 1930 in the western Adriatic Sea, suggesting preferable post-depositional mobilization of lighter congeners.

After the first detection of PCBs, historical concentrations showed an increasing trend until the middle of the 1950s in the Adriatic Sea sediments from the Po River prodelta (core J25), Ancona (core AN2) and Bari (core BA5) except in the Gargano Promontory (core GG2), following the escalation of PCBs use after their production started.

In the Po River prodelta sediments (core J25), a PCB peak concentration of 8.1 ng g^{-1} was detected at the beginning of the 1950s, corresponding to a major Po River's flood occurred in November 1951. According to data obtained from the Italian Regional Agency for Environmental Protection and Control (ARPA), a mean discharge close to 8000 m^3 s^{-1} was registered during this heavy flood event. Large floods can mobilize upstream PCB sources, resulting in inputs of contaminated sediments, and thus affect PCB distribution (Mourier et al., 2014).

Maximum peak concentrations of 9.0 ng g^{-1}, 3.9 ng g^{-1}, 2.2 ng g^{-1}, and 3.2 ng g^{-1} occurred between 1960s and the 1980s in the Po River prodelta (core J25), Ancona (core AN2), the Gargano Promontory (core GG2) and Bari (core BA5), respectively, coinciding with the maximum PCB production worldwide and with the predicted trends on PCB consumption and emission in Italy (Breivik et al., 2002b; Breivik et al., 2007) (Fig. 4). This period also corresponds to the beginning of the production of PCB by the Caffaro industry in northern Italy (Breivik et al., 2002b).

In the Po River prodelta sediments, high-chlorinated PCB predominates especially between the 1970s and the mid 1980s, accounting for approximately 50% of the total PCB mixture ($\sum_{28}$ PCBs) and corresponding to the time interval of maximum production in Italy (Figs. 2 and 3). Although low-chlorinated PCB predominates in Ancona, the Gargano Promontory and Bari cores making up from ~60 to nearly 100% of the total PCBs mixture, an increase of high-chlorinated PCBs occurred during the years of maximum production in these areas of the western Adriatic Sea.

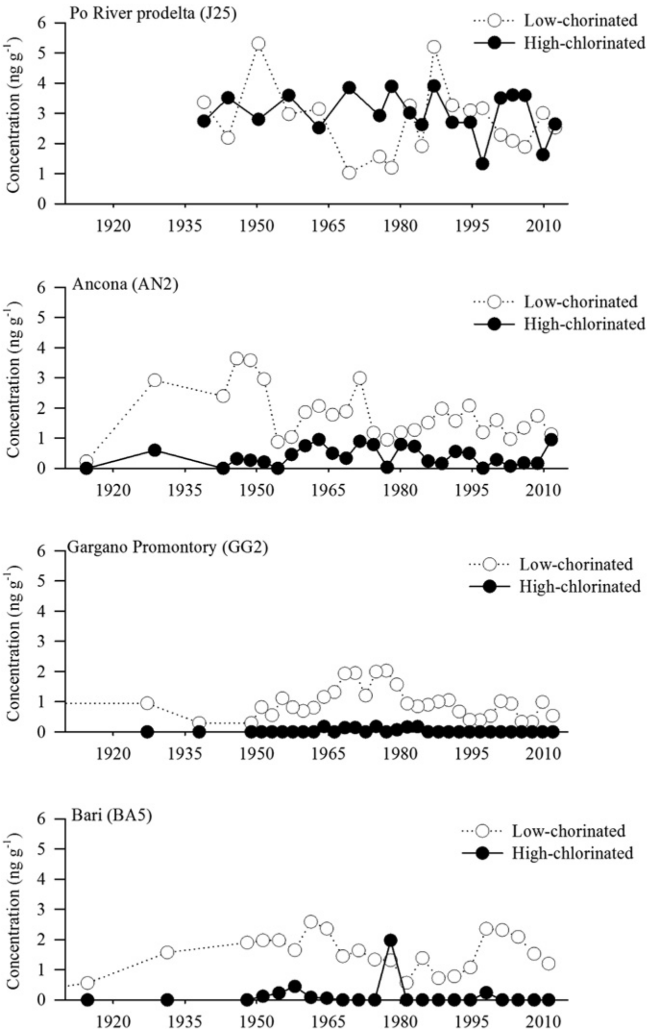

Fig. 3. Distribution of low-chlorinated (di-, tri-, tetra- and penta-CB) and high-chlorinated PCBs (from hexa- to deca-CB) in ng g^{-1} in sediment cores from the western Adriatic Sea.

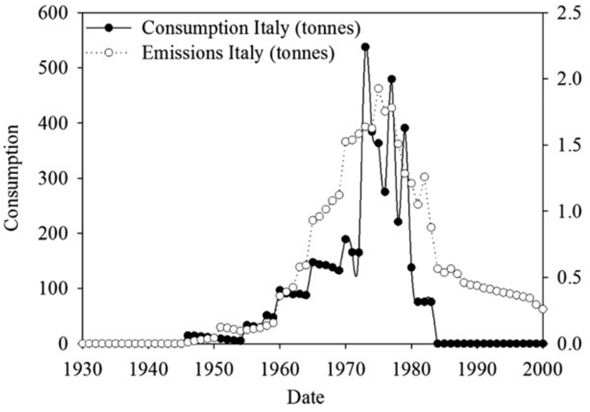

Fig. 4. Predicted temporal trends on PCB consumption and emission in Italy (according to data provided by Breivik et al., 2002a, 2007).

The sediments from the Po River prodelta, Ancona, the Gargano Promontory and Bari registered respective reductions of ~40%, ~ 50%, ~ 60%, ~ 80% in recent years, when compared to PCB peak concentrations detected between 1960s and the 1980s. The lower concentrations found in the upper layers corresponding to the last two decades most likely reflected ban/restriction on PCB production and use in Italy due to incoming European regulations, which started to be adopted in 1976 (Tolosa et al., 1997). Despite the general decreasing trends on PCB concentrations in the past decades, their fluxes and concentrations seem to be reaching a steady state in more recent years (end of the 1990s and early 2000s), suggesting that a further reduction of PCB levels in the next years is unlikely. According to Breivik et al. (2007), PCB concentrations will return to decrease significantly after 2050, when PCBs are expected to be completely out of use. Furthermore, the whole drainage basin of the Po River would act a transient repository for PCBs, which can be slowly released over time, as occurred with transport and accumulation of radiocesium in the North Adriatic Sea following the Chernobyl accident (Frignani et al., 2004).

Although the Po River has been considered the major source of PCBs in the western Adriatic Sea, minor local inputs may also be present in Ancona and Bari areas. Actually, Ancona and Bari are urban centers sheltering two of the most important commercial and passenger harbors of the central and southern Adriatic (Mali et al., 2015), and the human activities in these coastal areas seem to be affecting PCB inputs and sediment quality. Relative higher concentrations of PCBs and other contaminants had been detected especially around the Bari port area (e.g. Guzzella and De Paolis, 1994; Giandomenico et al., 2013; Mali et al., 2015).

3.5. PCB inventories

PCB inventories were assessed to estimate the total mass of PCBs in the sediment cores. Inventories can also be used to evaluate the potential of sediments as a new source of contamination to the marine ecosystem in the region. The inventories (ng cm^{-2}) were calculated as follows:

$$Inventory = \sum C_i d_i \rho_i$$

where C_i is the concentration of $\sum_{28}$ PCBs in sediment layer i (ng g^{-1}), d is the thickness of the sediment layer i (cm) and ρ_i is the dry mass of the sediment layer i (g cm^{-3}; Mai et al., 2005). The PCB concentrations for unanalyzed intervals were estimated by linear interpolation of adjacent measured intervals.

The PCB inventories were estimated among the sediment layers corresponding from 1930 (first PCB production) until recent years. The inventory of PCBs was 256 ng cm^{-2} at the Po River prodelta (core J25), 63 ng cm^{-2} in Ancona (core AN2), 37 ng cm^{-2} in Bari (core BA5), 35 ng cm^{-2} at the Gargano Promontory (core GG2) and 2.5 ng cm^{-2} at the Gondola slide (core DE15bis) (Table 1). The estimated inventory of PCB in the Po River prodelta is ~4 to 7 times greater in comparison to the middle and southern Adriatic, respectively, and about 100 times higher than the inventory obtained in the deep Adriatic Sea at the Gondola slide mud waves. The estimated PCB inventories are in agreement with the detected distribution trends of total PCB in the Adriatic Sea.

PCB inventories in the Po River prodelta are higher than those detected in Venice Lagoon, Italy (32–80 ng cm^{-2}; Mugnai et al., 2011) and in heavily polluted tropical bays in the Philippines and in the upper Gulf of Thailand (47–92 ng cm^{-2}; Kwan et al., 2014). On the other hand, PCB inventories as high as 1310 ng cm^{-2} were found in the Pearl River Delta, China, a well-known polluted site and active area for deposition of sediment-bound contaminants (Mai et al., 2005). PCB inventories in the Po River prodelta are similar to the average values reported for the top 2-cm sediments from Santa Monica Bay (USA) and for dated sediment cores from English lakes (80 ng cm^{-2} and ~270 ng cm^{-2}, respectively; Venkatesan et al., 2010; Yang et al., 2016).

4. Conclusions

This work provides the first extensive data set on the sources, historical patterns and inventories of PCBs in sediments from western Adriatic Sea. Total PCB concentrations, especially high-chlorinated congeners, decrease with distance from the Po River prodelta southward, suggesting the Po River outflow to be a major contributor of PCB inputs to sediments in the western Adriatic Sea. PCB inventories, OC and C/N spatial trends corroborate this hypothesis. The occurrence of high-chlorinated PCB congeners at the Gondola slide suggests that the cascading process of the NAdDW could quickly transfer particle-bound contaminants such as PCBs from the north to the deep Adriatic Sea.

Historical trends of PCBs in the Adriatic Sea coincided with their past use and industrial production. Despite the relatively low concentrations detected, this work provides a new insight on the historical and recent PCB contamination status in the western Adriatic Sea at a basin level. Further studies including priority and emerging contaminants are warranted to fully characterize the contamination status of the Adriatic Sea.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2016.04.086.

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