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

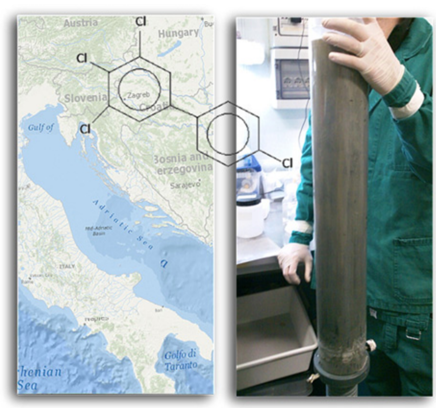
Tatiane Combi [a,*], Stefano Miserocchi [b], Leonardo Langone [b], Roberta Guerra [a,c]

[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

HIGHLIGHTS

- PCBs were determined in recent and dated sediments from the western Adriatic Sea.
- Unprecedented data of PCB levels, historical trends and inventories were assessed.
- PCB historical trends corresponded to their production and use over time.
- Congener composition indicates the Po River as the major contributor of PCBs.
- High-chlorinated PCBs in the deeper Adriatic suggest influence of cascading process.

GRAPHICAL ABSTRACT



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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 ($\sum_{28}$ PCBs) ranged from <LOD (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.

1. Introduction

Polychlorinated biphenyls (PCBs) are a classical group of persistent organic pollutants (POPs) that were extensively used worldwide since

* Corresponding author.
E-mail address: tatiane.combi4@unibo.it (T. Combi).

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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