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**Historical sedimentary deposition and flux of PAHs, PCBs and DDTs in sediment
cores from the western Adriatic Sea**

*Tatiane Combi^{1,2}, Marina G. Pintado-Herrera³, Pablo A. Lara-Martín³, Marília L.
Rocha², Stefano Miserocchi⁴, Leonardo Langone⁴, Roberta Guerra^{2,5}

¹Universidade Federal da Bahia, Instituto de Geociências, Departamento de
Oceanografia. Rua Barão de Jeremoabo, 40170-020 Salvador, Bahia, Brazil.

² Centro Interdipartimentale di Ricerca per le Scienze Ambientali, Università di
Bologna, Via Sant'Alberto 123, 48123 Ravenna, Italy

³ Departamento de Química-Física, Facultad de Ciencias del Mar y Ambientales,
Universidad de Cádiz, 11510 Puerto Real, Cádiz, Spain

⁴ Istituto di Scienze Marine, Consiglio Nazionale delle Ricerche, 40129 Bologna, Italy

⁵ Dipartimento di Fisica e Astronomia, Università di Bologna, Bologna, Italy

***Corresponding author**

E-mail address: tatiane.combi@ufba.br

Abstract

The sources and depositional history of polycyclic aromatic hydrocarbons (PAHs) and organochlorine compounds (OCs) over the last century were investigated in sediment cores from the North Adriatic Sea (Po River prodelta) and the South-Western Adriatic Margin (SWAM). Contaminant concentrations were higher in the Po River prodelta. $\Sigma_{16}\text{PAHs}$ ranged from 193 to 533 ng g⁻¹, $\Sigma_5\text{PCBs}$ ranged from 0.9 to 5.2 ng g⁻¹ and ΣDDTs (*p,p'*-DDD + *p,p'*-DDE) ranged from 0.1 to 2.5 ng g⁻¹. In the SWAM, ΣPAHs ranged from 11 to 74 ng g⁻¹ while ΣPCB and ΣDDT concentrations were close to the MQL. Accordingly, contaminant fluxes were much higher in the northern (mean values of 152 ± 31 ng cm² y⁻¹ and 0.70 ± 0.35 ng cm² y⁻¹ for PAHs and OCs, respectively) than in the southern Adriatic (2.62 ± 0.9 ng cm² y⁻¹ and 0.03 ± 0.02 ng cm² y⁻¹ for PAHs and OCs, respectively). The historical deposition of PAHs seemed to be influenced by the historical socioeconomic development and by changes in the composition of fossil fuel consumption (from petroleum derivatives to natural gas) in Italy from the end of the 19th century to the present. Similarly, vertical variations in DDT concentrations matched its historical use and consumption in Italy, which started around in the mid- late 1940s to fight typhus during the II World War. Contaminant concentrations detected in sediments does not seem to pose ecotoxicological risk for marine organisms in the Adriatic Sea.

Key-words: Persistent organic pollutants (POPs); Sediment cores; Fluxes; Western Adriatic Sea; Eco-toxicological implications.

1. Introduction

Persistent organic pollutants (POPs) are among the most concerning groups of legacy contaminants due to well-known characteristics as high persistence in the environment, hydrophobicity and toxicity (Lohmann et al., 2007). Among POPs, the organochlorine compounds (OCs), including polychlorinated biphenyls (PCBs) and dichlorodiphenyl-trichloroethanes (DDTs), are the most relevant (Jones and de Voogt, 1999).

PCBs are commonly considered as key representatives of the “industrial” POPs and were massively produced from the 1930s to the beginning of the 1980s in industrialized countries (Breivik et al., 2004; Hosoda et al., 2014). In spite of the production and use ban, PCBs are still in use (in closed systems, e.g., electrical transformers) and broadly distributed in the environment (Hornbuckle and Robertson, 2010). In turn, DDT is the best known and one of the most widely used pesticides in the world, with an estimated production around 50 million kg per year in the mid-1950s, especially because of its wide spectrum, long-lasting properties, and low cost in comparison to arsenicals and other inorganic insecticides (Matsumura, 2009). Currently, DDT is still in use in some countries in the Southern Hemisphere, though current world usage is small ($\sim 1\text{kt y}^{-1}$) compared with historical use ($>40\text{kt y}^{-1}$) from 1950 to 1980 (de Boer et al., 2008; Geisz et al., 2008).

Due to their long-range atmospheric transport potential and harmful effects on man and wildlife, regulatory efforts and international agreements have been made in past decades in order to reduce future environmental burdens (Breivik et al., 2004; Vallack et al., 1998). At global scale, POPs are regulated by the Stockholm Convention under which the signatory countries are legally required to eliminate the production, use, and emissions of POPs, with the ultimate goal of reducing human and ecosystem exposure (Holoubek and Klánová, 2008; Nizzetto et al., 2010). Parallel efforts have been made at

European level; for instance the recent Directive 2013/39/EU established a list of 45 substances identified for priority action at Union level, including some POPs as polychlorinated biphenyls (PCBs) and dichlorodiphenyl-trichloroethanes (DDTs), and some polycyclic aromatic hydrocarbons (PAHs) (European Commission, 2013; Viganò et al., 2015).

These regulatory actions have led to the reduction or elimination of major primary sources associated with the production and use of POPs, followed by a gradual decline on environmental levels of these contaminants over time, especially after the 1980's (Francu et al., 2009; Smith et al., 2009; Combi et al., 2016; Neves et al., 2018). However, there are still ongoing primary releases from diffuse sources that are difficult to target for reduction or elimination, such as volatilization from old stockpiles or from old equipment that is still in use (Breivik et al., 2002; Nizzetto et al., 2010). Additionally, these compounds are highly persistent in the environment and continue to be found in different environmental media, and their current levels are not expected to decrease significantly within the next decades (Breivik et al., 2007). Evidence of this unlike decline or even an increase in DDTs and/or PCBs levels has been recently observed in the Arctic Fjords, glaciers and snow (Bartlett et al., 2019; Pouch et al., 2017; Garmash et al., 2013), in the Baltic Sea (Sobek et al., 2015), the Gulf of Thailand (Kwan et al., 2014), and the Korea Strait (Guerra et al., 2019), due to unintentional sources released from by-products of manufacturing (e.g. paint pigments; Hu and Hornbuckle, 2010), from thermal sources (e.g. steel making processes; Baek et al, 2010) and e-waste (Breivik et al., 2016), or from melting glaciers and the cryosphere affected by climate change-related processes (Sun et al., 2018; Pavlova et al., 2015). Therefore, it is essential to understand the temporal trends of contaminant loads into the

environment, in order to both assess the effects of environmental legislation and to identify potential old and new sources of contamination (Kannan et al., 2005).

Although PAHs as not listed as POPs, they are recognized as priority substances for environmental monitoring especially due to environmental risks associated with these compounds, which are related to the high toxicity and carcinogenic character of several individual PAHs. A wide variety of PAHs are ubiquitously found in the environment mostly as a result of the incomplete combustion of organic material (pyrolytic PAHs) and storm runoff, industrial discharges and petroleum spills (petrogenic PAHs) (Alebic-Juretic, 2011). Thus, understanding the pollution levels of PAHs and their source identification is of significant environmental concern.

The aim of this work is to reconstruct the historical inputs and estimate the annual fluxes of PCBs, DDTs and PAHs in sediment cores from: (a) a coastal region subject to intense urban, agricultural and industrial pressures in the North Adriatic Sea (Po River prodelta); and (b) a deep-sea area on the South-Western Adriatic Margin (SWAM) which represents the ultimate sink of sediment coming from the Po river system. This work is part of the PERSEUS EU FP7 Project (Policy-oriented Marine Environmental Research in the Southern European Seas), which presented as one of the main goals the understanding of the contaminants transfer of contaminants from coastal areas to deep sea sediments along Mediterranean margins.

2. Material and methods

2.1. Study area and sediment cores sampling

The Adriatic Sea is a semi-enclosed basin connected to the Mediterranean Sea through the Strait of Otranto (Gomiero et al., 2011; Manca et al., 2002). While the northern and middle Adriatic are relatively shallow regions (up to ~270 m water depth), the southern Adriatic can reach up to 1200 m depth in the South Adriatic Pit (Artegiani et al., 1997; Turchetto et al., 2007). The main water masses in the Adriatic Sea are: Adriatic Surface Water (ASW) flowing on the western Italian side; the Levantine Intermediate Water (LIW), coming from the eastern Mediterranean; the North Adriatic Deep Water (NAdDW), formed over the northern shelf; and the South Adriatic Deep Water (SADW), formed in the southern Adriatic (Artegiani et al., 1997; Manca et al., 2002; Turchetto et al., 2007).

The water circulation in the Adriatic Sea has three major components: river runoff derived mainly from the Po river; wind and heat forcing at the surface, producing deep-water masses in the northern and southern Adriatic; and the Otranto Channel forcing (Artegiani et al., 1997). The water circulation as well as the transport of materials in the Adriatic basin is very dependent on thermohaline factors. As a result, riverborne material is distributed southwards, accumulating in a continuous belt of deltaic and shallow-marine deposits which forms the late-Holocence mud wedge along the western Adriatic shelf (Frignani et al., 2005; Tesi et al., 2013). Another relevant area for material accumulation is the Bari canyon system, in the southern Adriatic. The Bari canyon system receives material from the northern Adriatic, including the Po river, especially through the cascading of the North Adriatic Dense Water (NAdDW) in the area (Langone et al., 2016; Turchetto et al., 2007).

In the context of the task 'ADREX: Adriatic and Ionian Seas Experiment' within the PERSEUS project, sediments were collected in the western Adriatic Sea in October 2014 on board the O/V OGS Explora at the following key stations: the Po River

prodelta (station 9; ~27 m water depth); off the Bari Canyon (station 1; ~709 m water depth); and in a giant sediment drift (Foglini et al., 2016) in the centre of the South Adriatic (station 2; ~1040 m water depth; Figure 1). Undisturbed sediment cores (length ≤ 50 cm; diameter: 10 cm) were retrieved using a cylindrical box-corer or the gravity sediment corer SW104, and sectioned onboard at 1-2 cm intervals. Sediments were placed into pre-cleaned glass containers and stored at -20 °C until processing and analysis.

2.2. Sediment characteristics

Sediment samples 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 H₂O₂ and wet sieving at 63 μ m to separate sands from fine fractions. Total carbon (TC) and total nitrogen (TN) content were determined by elemental analysis (EA) of combusted aliquots with a Fison CHNS-O Analyzer EA 1108, and organic carbon (C_{org}) was measured on decarbonated samples (1 M HCl). Stable isotopic analyses of organic C ($\delta^{13}\text{C}$) were carried out on the same samples using a FINNIGAN Delta Plus mass spectrometer directly coupled to the FISIONS NA2000 EA by means of a CONFLO interface for continuous flow measurements.

2.4. Extraction and clean-up

Sediments were extracted using an accelerated solvent extraction ASE 200 system (Dionex, USA) according to the extraction and in-cell clean-up method optimized by

Pintado-Herrera et al. (2016a). Briefly, the extraction cells were prepared with 1 g of activated alumina (150°C for 16 hours; USEPA method 3610b) and 0.5 g of activated copper powder. Approximately 4 g of air-dried and milled sediments were homogenized with 1g of alumina and placed into the extraction cells. A mixture of deuterated compounds was added to the sediments before extraction to account for matrix interferences. The extraction procedure consisted of three static extraction cycles using dichloromethane, where the samples were pre-heated for 5 minutes and extracted for 5 minutes in each cycle at a temperature of 100°C and a pressure of 1500 psi. The eluates were evaporated to dryness and re-dissolved in 0.5 mL of ethyl acetate. The final extracts were centrifuged (10000 rpm for 10 minutes) and filtered in polytetrafluoroethylene filters (PTFE; 0.22 μm pore size) to remove possible interferences.

2.5. Instrumental analysis

Separation, identification and quantification of target compounds were performed using gas chromatography (SCION 456-GC, Bruker) coupled to a triple quadrupole mass spectrometer equipped with a BR-5ms column (length: 30 m, ID: 0.25 mm, film thickness: 0.25 μm). The oven temperature was programmed to 70 °C for 3.5 min, increasing at 25 °C min⁻¹ to 180 °C, increasing at 10 °C min⁻¹ to 300 °C, holding this temperature for 4 min. Internal standards (mixture of deuterated compounds) were added to the samples prior to the injection. Calibration curves were prepared for each target compound at different concentrations (from 5 to 500 ng g⁻¹). Target compounds were identified and quantified by comparison of retention times and two transitions of each analyte (one for quantification and one for confirmation) of the samples with external standard solutions.

The compounds analyzed in this study were (i) the 16 priority PAHs: naphthalene (Na), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flo), phenanthrene (Phe), anthracene (An), fluoranthene (Fl), pyrene (Py), benzo[a]-anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IcdP), dibenzo[a,h]anthracene (DahA), and benzo[g,h,i]perylene (BghiP); (ii) PCBs (PCB52, PCB138, PCB153, PCB180 and 101; and (iii) dichlorodiphenyltrichloroethane and derivatives (*p,p'*-DDT, *p,p'*-DDD, *p,p'*-DDE). Results are given as sum of congeners for PCBs, sum of the 2 DDT metabolites (*p,p'*-DDE + *p,p'*-DDD) and DDT for DDTs, and sum of 16 unsubstituted compounds for PAHs (ng g⁻¹).

2.6. Quality assurance and quality control (QA/QC)

Procedural blanks were performed for each extraction series of 10 samples using alumina and analyzed in the same way as samples. Method quantification limits (MQL) were determined for each analyte as 3 times the signal to noise ratio in spiked sediment samples and were between 0.01 ng g⁻¹ (PCB 138) and 1.8 ng g⁻¹ (indeno[123-cd]pyrene) depending on the target compound. Further information on the methodology, standards and other reagents can be found in Pintado-Herrera et al. (2016a).

2.7. Data analysis

Principal component analysis (PCA) was used to depict the vertical differences among the groups of contaminants (DDTs, PCBs, and PAHs) and sediment characteristics (fine sediments and C_{org}) in the sediment cores. All variables were centered and scaled before performing the PCA. The analysis and graph were produced using the R programming environment (R Core Team, 2019).

2.8. Sediment dating and fluxes

Since information on sediment accumulation rates (SARs) have been extensively assessed in the northern Adriatic Sea, different datasets were combined based on triangle-based linear interpolation (Frignani et al., 2005; Palinkas and Nitttrouer, 2007; Tesi et al., 2013) to estimate the SARs for the sediment core from the Po River prodelta (station 9). Conversely, information on strata chronologies in the deep Adriatic is rather scarce. Thus, sediment cores from the southern Adriatic (Stations 1 and 2) were 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 SARs (0.107 cm y^{-1} at Station 1, 0.100 cm y^{-1} at Station 2, and 0.52 cm y^{-1} at Station 9) were used to estimate the date for each section of the sediment cores as follows:

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

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.

Contaminant fluxes ($\text{ng cm}^{-2} \text{ y}^{-1}$) were estimated as

$$C_i \times r \times \rho_i$$

where C_i is the concentration of contaminants ($\sum\text{PCBs}$, $\sum\text{DDTs}$, and $\sum\text{PAHs}$) in sediment layer i (ng g^{-1}), r is the SAR in the sediment core (cm y^{-1}) and ρ_i is the bulk dry density of the sediment layer i (g cm^{-3}).

2.9. Ecological Risk Assessment

In order to assess the potential ecotoxicological risks posed by contaminants present in sediments from the Adriatic Sea, we compared our data with four sets of Sediment Quality Guidelines (SQGs): Effects Range-Low value (ERL), Effects Range-Median value (ERM), Probable Effects Level (PEL), and Threshold Effects Level (TEL) (Long et al., 1995; Macdonald et al., 2000). Additionally, mean SQG quotients were calculated to evaluate the combined effects that the presence of a mixture of organic contaminants in sediments may pose to aquatic organisms (Macdonald et al., 2000; Jafarabadi et al., 2017b). Mean ERM and mean PEL (i.e., m-ERM and m-PEL) were calculated as follows:

$$m - SQG = \frac{\sum \frac{C_i}{SQG_i}}{n}$$

Where C_i concentration of each contaminant in the sample; SQG_i is the SQG for the contaminant; and n is the number of considered contaminants. Mean SQGs were calculated for: (i) individual PAHs (Na, Acy, Ace, Flo, Phe, An, Fl, Py, BaA, Chr, BaP, and DahA) and (ii) \sum PCBs, \sum DDTs, and \sum PAHs.

3. Results

3.1 Sediment characteristics

Sediment cores were collected in areas where preferential accumulation of fine-grained sediments was previously reported (Frignani et al., 2005; Tesi et al., 2007). Accordingly, fine sediments (i.e. silt + clay) were detected in percentages above 90% in the analyzed samples. Vertical distribution of fine sediments was relatively constant in the sediment cores, with mean values of $96.9 \pm 1.3\%$ at station 1 (off the Bari canyon), $97.4 \pm 0.7\%$ at station 2 (sediment drift), and $98.5 \pm 1\%$ at station 9 (Po River prodelta,

Table 1). In general, organic carbon (C_{org}) was also constant (mean values of $0.5 \pm 0.06\%$, $0.45 \pm 0.08\%$, and $0.9 \pm 0.09\%$ at station 1, station 2, and station 9, respectively), with a slight increase from the bottom to the top sections of the sediment cores.

3.2 Organochlorine compounds

The highest concentrations of organochlorine compounds (OCs) were detected in the Po River prodelta. Total PCBs ($\sum_5 PCBs$) ranged from 0.9 to 5.2 ng g^{-1} ($2.4 \pm 0.8 \text{ ng g}^{-1}$), with predominance of congeners PCB 138 and PCB 180, which accounted for 45% and 20% of total PCBs, respectively. $\sum DDTs$ (p,p' -DDD + p,p' -DDE) ranged from 0.1 to 2.5 ng g^{-1} ($1.0 \pm 0.4 \text{ ng g}^{-1}$). The isomer p,p' -DDE, which is the degradation product of p,p' -DDT under aerobic conditions, was the prevalent compound corresponding to ~70% of total DDTs.

In the deep southern Adriatic, OCs levels were close to the MQL (0.01 to 0.06 ng g^{-1} for PCBs and 0.04 to 0.3 ng g^{-1} for DDTs) and were detected in roughly half of the samples. Only PCB congeners 138 and 180 were detected in measurable amounts and their sum ranged between 0.1 and 2.1 ng g^{-1} ($0.5 \pm 0.3 \text{ ng g}^{-1}$), and between $<DL$ and 1.4 ng g^{-1} ($0.3 \pm 0.3 \text{ ng g}^{-1}$) off the Bari canyon and at the sediment drift (stations 1 and 2), respectively. The $\sum DDTs$ ranged from $<DL$ to 2.1 ng g^{-1} ($0.6 \pm 0.6 \text{ ng g}^{-1}$) at station 1 and from $<DL$ to 0.7 ng g^{-1} ($0.3 \pm 0.3 \text{ ng g}^{-1}$) at station 2.

3.3 PAHs

PAHs were the prevalent contaminants in the sediment cores from the Adriatic Sea and were detected in all sediment strata. The concentrations of $\sum_{16} PAHs$ ranged from 24 to

74 ng g⁻¹ (48.3 ± 16 ng g⁻¹) in sediment core 1 (off the Bari canyon; Figure 2); from 11 to 49 ng g⁻¹ (25 ± 9 ng g⁻¹) in sediment core 2 (sediment drift; Figure 3); and from 193 to 533 ng g⁻¹ (mean ± SD of 363 ± 59 ng g⁻¹) in sediment core 9 (Po River prodelta; Figure 4).

The relative abundance of individual PAHs was calculated as their concentrations in relation to the average \sum_{16} PAHs concentration over the entire depth of sediment cores to evaluate sedimentary PAH compositions and potential spatial differences (Liu et al., 2012). PAHs in sediments of the western Adriatic Sea exhibited a quite uniform distribution, with a predominance of high-molecular weight PAHs (HMW: 4-6 rings). From these, 5- and 6-ring PAHs (BbF, BkF, BaP, IcdP, DahA, and BghiP) accounted for 50 to 65% of total PAHs, while 4-ring PAHs (Fl, Py, BaA, and Chr) accounted for 20 to 33%. The presence of low-molecular weight PAHs (LMW: Na, Acy, Ace, Flo, Phe, and An) PAHs was somewhat higher in the sediment taken in the sediment drift (station 2; ~30%) in comparison to sediment cores taken off the Bari canyon (station 1; 15%) and in the Po River prodelta (station 9; 13%). The ratio between LMW and HMW PAHs ranged from 0.1 to 1.4 in the sediment cores.

Diagnostic ratios have been widely used for interpreting PAHs composition and sources. Since ratios calculated from LMW PAHs can be altered during transport from sources to receptor sites (Cai et al., 2016), only the Fl/(Fl + Py) and IcdP/(IcdP + BghiP) ratios are discussed in our study. Values of Fl/(Fl + Py) and IcdP/(IcdP + BghiP) were usually close to or above 0.5 in the southern Adriatic (stations 1 and 2). In the Po River prodelta (station 9), the Fl/(Fl + Py) ratio was generally above 0.5 while the IcdP/(IcdP + BghiP) ratio was between 0.4 and 0.5 (Figure S1 from Supplementary Material).

3.4 Fluxes and vertical distribution of OCs and PAHs

Similarly to concentration data, annual fluxes of OCs were lower in the southern Adriatic (from 0 to 0.15 ng cm² y⁻¹ and from 0 to 0.1 ng cm² y⁻¹ in stations 1 and 2, respectively) in comparison to the northern Adriatic (0.02 to 2.2 ng cm² y⁻¹; Table 1). Annual fluxes and concentrations of OCs (\sum_5 PCBs and \sum DDTs) followed a similar vertical pattern in the three sediment cores (Figures 2, 3, and 4). In general, OCs were un-detectable or negligible before the 1940s, when they first occurred in sediments from the western Adriatic, followed by an increasing trend up to the middle/late 1970s - early 1980s. This sediment stratum displayed the highest concentrations of \sum_5 PCBs (2.1 ng g⁻¹, 0.7 ng g⁻¹, and 5.2 ng g⁻¹ in stations 1, 2, and 9) and \sum DDTs (2.1 ng g⁻¹, 0.7 ng g⁻¹, and 2.5 ng g⁻¹ in stations 1, 2, and 9, respectively). After the 1980s, annual fluxes and concentrations of OCs decreased upwards until recent sediments, where PCBs presented concentrations of 0.5 ng g⁻¹, <LQ, and 2.7 ng g⁻¹ and DDT presented concentrations of 0.7 ng g⁻¹, 0.6 ng g⁻¹, and 0.9 ng g⁻¹ in stations 1 (off Bari canyon), 2 (sediment drift), and 9 (Po river prodelta), respectively.

PAHs presented the highest fluxes (152 ± 31 ng cm² y⁻¹) in the Po River prodelta (station 9), followed by off the Bari canyon (station 1; 3.2 ± 0.9 ng cm² y⁻¹) and the sediment drift (station 2; 1.8 ± 0.5 ng cm² y⁻¹). PAHs fluxes and concentrations presented similar patterns along the sediment cores. The oldest sections of the sediment cores (before 1940) displayed the lowest mean concentrations of \sum_{16} PAHs (32 ± 4 ng g⁻¹, 16 ± 4 ng g⁻¹, and 227 ± 26 ng g⁻¹ in, off the Bari canyon, the sediment drift and the Po River prodelta (stations 1, 2, and 9, respectively). Afterwards, mean concentrations of \sum_{16} PAHs increased to 62 ± 8 ng g⁻¹, 48 ± 1 ng g⁻¹, and 392 ± 32 ng g⁻¹ in sediment cores off the Bari canyon (station 1), in the Sediment rift (station 2), and in the Po River prodelta (station 9), respectively. Mean concentrations of \sum_{16} PAHs show a somewhat

decrease in this period, reaching $66 \pm 12 \text{ ng g}^{-1}$ in station 1, $38 \pm 8 \text{ ng g}^{-1}$ in station 2, and $348 \pm 12 \text{ ng g}^{-1}$ in station 9.

3.5 Ecological Risk Assessment

Data regarding ecological risk assessment in the Adriatic Sea is presented in Tables S1 and S2 from Supplementary Material. In general, contaminant levels in our study did not exceed the proposed SQGs (ERL, ERM, TEL, and PEL), except for dibenzo[a,h]anthracene (DahA), which was above TEL in 88% of the samples from the Po river prodelta (station 9). Mean-ERM and mean-PEL for individual PAHs ranged between 0.01 and 0.02 and between 0.02 and 0.04, respectively. For the Σ PCBs, Σ DDTs, and Σ PAHs, m-ERM ranged from <0.01 to 0.01 and m-PEL ranged from 0.01 to 0.02.

4. Discussion

4.1. Levels of OCs and PAHs in sediments

Few studies have reported the temporal distribution of organic contaminants along the Adriatic Sea. PAHs levels detected in the Po River prodelta in our study were slightly higher when compared to those previously detected in the same area (102 to 346 ng g^{-1} ; Guzzella and Paolis, 1994), whereas PCBs and DDTs concentrations were lower and/or comparable to previous levels (Caricchia et al., 1993; Combi et al., 2016). Regarding the deep southern Adriatic, such data are even scarcer and PCB levels in our study were slightly higher than previously reported ($< \text{DL-}0.2 \text{ ng g}^{-1}$ for Σ_5 PCBs; Combi et al., 2016).

PAH concentrations in our study were lower in comparison to those reported in sediment cores from coastal areas subject to industrial activities such as the northwest coast of Spain (Pérez-Fernández et al., 2016) and Izmit Bay, Turkey (Giuliani et al., 2017). While PAH levels in the Po river prodelta were higher in comparison to less-impacted and open sea areas (Table 2), concentrations in the southern Adriatic were comparable to those detected in the continental shelf of the East China Sea (Cai et al., 2016), the Gulf of Thailand (Boonyatumanond et al., 2007), and in remote areas such as the Arctic (Zaborska et al., 2011) and Antarctica (Martins et al., 2010b). Overall, the levels of OCs in our study were comparable to those detected in the East China Sea, the Gulf of Thailand, and the Western Barents Sea (Boonyatumanond et al., 2007; Cai et al., 2016; Zaborska et al., 2011) whilst PCBs were fairly below the maximum values reported in Izmit Bay (Giuliani et al., 2017) and Antarctica (Combi et al., 2017).

4.2 Source assessment

PCB congeners detected in our study are the main contributors to the commercial mixtures Aroclor 1260 and Aroclor 1254 (Schulz et al., 1989), which were the most frequently imported mixtures in Italy until the 1980s, being used mainly in electrical transformers and hydraulic fluids (Parolini et al., 2010; Pozo et al., 2009). As for DDTs, in developed countries, where DDT has been banned for a long time, higher amounts of DDE in comparison with DDD and DDT have been reported in the aquatic environment (Bossi et al., 1992; Mandalakis et al., 2014; Viganò et al., 2015) and may indicate that the process of on-land weathering tends to favor the formation and preservation of DDE, as compared to DDD (Zhang et al., 2002).

The incomplete combustion or pyrolysis of organic material (e.g. biomass, waste, fossil fuels) under high temperatures is one of the main sources of PAHs, as well as natural

and anthropogenic petroleum spillages (Magi et al., 2002; Readman et al., 2002). Generally, pyrolytic sources are depleted in low-molecular weight PAHs (LMW: 2–3 rings) and enriched in high-molecular weight PAHs (HMW: 4–6 rings) leading to LMW/HMW ratio < 1 (Merhaby et al., 2015; Jafarabadi et al., 2017). Thus, the ratios between LMW and HMW PAHs reported in our study indicate the predominance of pyrolytic sources in the western Adriatic Sea. Similarly, the diagnostic ratios $Fl/(Fl + Py)$ and $IcdP/(IcdP + BghiP)$ indicated pyrolytic sources of PAHs related to biomass combustion in the southern Adriatic (stations 1 and 2). A separated cluster can be identified for the Po River prodelta (station 9; Figures S1 and S2 from Supplementary Material) probably because, in addition to biomass combustion, petroleum combustion also represented a source of PAHs in this sediment core.

4. 3 Historical records of PAHs, PCBs and DDTs in the Western Adriatic Sea

PCA can provide insights on relationships among the three groups of contaminants and sediment characteristics, allowing the recognition of similarities and differences among them. PCA (Figure 5) revealed two factors in our study, with PC1 explaining 57.5% of the total variation and mostly related to increasing concentrations of DDTs, PCBs, C_{org} , and PAHs.

PC1 strongly controls the variability between the sediment cores from the southern (stations 1 and 2) and northern Adriatic (station 9), the latter being mostly related to higher concentrations of all the above-mentioned variables. PC2 explained 19.5% of the total variation and was mostly related to vertical variations in the cores. The vector scores show a positive correlation between PCBs and C_{org} in the northern Adriatic, suggesting that the deposition of these compounds can be partly explained by their affinity for the organic matter.

Another factor influencing PCBs vertical patterns (Figures 2, 3, and 4) is related to the production and use of these compounds worldwide. PCB peak concentrations coincide with the beginning of the production of PCB by the Caffaro industry in northern Italy (1935-1983; Panizza and Ricci, 2002), as well as with the predicted trends on PCB consumption and emission in the country (Breivik et al., 2002, 2007; Combi et al. 2016).

Similarly, the historical deposition of DDTs in sediments from the western Adriatic Sea matches its historical use and consumption in Italy. DDTs first appeared in detectable concentrations in sediments in the mid- late 1940s following its first massive use to fight a severe typhus epidemics affecting the civilians and military personnel in 1943-1944 (Wheeler, 1946; Soper et al., 1947). After end of the II World War, DDT was extensively used in indoor and outdoor treatment mainly in the Central and Southern regions, major islands and North-eastern coastal areas, and continued into the mid-1950s and even later in some hyperendemic areas (Majori, 2012) as evidenced by the 1960s subsurface peak in the Po River prodelta station. In the 1970s and 1980s, agricultural use of DDT was banned in most developed countries including Italy, and this is reflected in the decreasing historical deposition observed in the sediments from the western Adriatic Sea (Figures 2, 3, and 4).

Vertical variations in PAH concentrations ($\Sigma_{16}\text{PAHs}$) and compositions (relative abundances of LMW and HMW PAHs) in our study seem to follow the shift in contamination sources influenced by the historical socioeconomic development and by changes in the composition of fossil fuel consumption in Italy from the 19th century to the present (Figure 6). Historical data on electricity production and consumption in Italy was obtained from reports of the Italian energy company (Terna Group, 2015).

Historical deposition of PAHs showed a common trend in sediment cores from the Po River prodelta (station 9), off the Bari canyon and at the sediment drift (stations 1 and 2). The lowest concentrations were reported in the bottom strata (end of the 1880s – beginning of the 1900s). This finding is consistent with the relatively low consumption and production of energy in Italy from the end of the 1800 until the Second World War (Malanima, 2011). In comparison to periods after ~1940, LMW PAHs were relatively more abundant in the oldest sections of the sediment cores (Figure S3 from Supplementary Material). These PAHs are usually generated by moderate temperature combustion processes such as biomass and coal burning in homes and small factories (Cai et al., 2016; Yunker et al., 2002). The predominance of LMW PAHs is particularly evident in the sediment core from the sediment drift (station 2), that dates back to the 1870's when Italy was almost completely dependent on biomass burning as a source of energy and firewood accounted for half of the total energy consumption (Malanima, 2006).

Afterwards, concentrations increased from the lower strata to the middle sections of sediment cores (1960s – 1990s). Σ PAH, Σ PCB and Σ DDT displayed a synchronous deposition with maximum peak values recorded in the mid-1970s in the Po prodelta station, and at the beginning of the 1980s for Σ DDT and Σ PAH in the South-Western Adriatic Margin (SWAM) stations. This period corresponds to the modern stage of economic and industrial development in Italy, the so-called “Economic Miracle” (~1945-1970), marked by mass motorization, switch from coal to oil, and industrial development (Romano et al., 2013). In this section, there is a change in the relative abundances of low- and high-molecular weight PAHs: whereas the former decreases, the latter increases until the middle of the 20th century (Figure S3 from Supplementary Material). Since HMW PAHs are usually generated during high-temperature

combustion of coal and petroleum (Cai et al., 2016; Yunker et al., 2002), this variation reflects a shift of contamination sources from domestic biomass burning to vehicle and industrial emissions as fossil fuels represented almost 50% of the energy used in Italy by the 1950s (Malanima, 2006). Historical shift from biomass to petroleum combustion is also revealed by variations on PAH ratios (Flt / Flt + Pyr; Figure S2 from Supplementary Material).

After the mid-1970s, the energy production was still growing but at a much lower rate (ten- and two-fold increase from 1945 to 1975 and from 1975 to 2014, respectively). Although natural gas was used since the end of the 19th century, it surpassed the use of coal in the 1970s (Malanima, 2006). In turn, relative proportions of HMW PAHs showed a slight decrease specially after the 1980's. In this period, the consumption of natural gas was still growing while the consumption of oil showed an important decrease (from 81 to 54% of fossil fuel consumption in Italy from 1970 to 2000; Malanima, 2006). This period is also marked by increasing consumption of cleaner energies (e.g. aeolian energy) (Malanima, 2006) and the beginning of environmental awareness and environmental legislation (Romano et al., 2013).

Contaminants deposition in the Po River prodelta (station 9) is influenced by episodic flood sedimentation (Palinkas and Nittrouer, 2007) (Figure 4). During the XX century, several flooding events with daily peak discharge above $8,000 \text{ m}^3\text{s}^{-1}$ occurred, specifically in 1926, 1928, 1951, 1976, 1994 and 2000, with the absolute maximum daily discharge observed on 20 May 1926 ($9,780 \text{ m}^3\text{s}^{-1}$; Zanchettin et al., 2008). ΣPAH , ΣPAH , ΣDDT presented the first onset in the beginning of the 1950s; according to data obtained from the Italian Regional Agency for Environmental Protection and Control (ARPA, 2014), a peak daily discharge of $8940 \text{ m}^3\text{s}^{-1}$ was registered during a major flood event in November 1951. Although concentrations started to decrease after the mid- late

1970's, a subsurface peak in Σ PAH, and to a lesser extent an increase in OCs concentrations, can be identified after a Po River's flood occurring in November 2000. This event represents the largest flood occurring in the previous century and recorded a mean daily maximum water discharge above $9,000 \text{ m}^3 \text{ s}^{-1}$ as well as the longest duration of high river discharge ($> 4,000 \text{ m}^3 \text{ s}^{-1}$) (Tesi et al., 2008). The signature of this flood event is clearly marked by the concurrent heaviest $\delta^{13}\text{C}$ signal, indicating the predominance of riverine sources within the same period (Miserocchi et al., 2007). Large floods can mobilize upstream contaminants sources, resulting in inputs of contaminated sediments, and thus affect pollutants distribution (Mourier et al., 2014). The OCs concentration reduction over time observed from the 1980s to the mid-late 1990s levelled off in the last two decades in the Po River prodelta, and concentrations of Σ DDT and Σ PCBs appear to be at or near a steady-state condition in the XXI century. The presence of DDD and DDE isomers, but not DDT, and more highly chlorinated PCBs (PCB 138 and PCB 180) seems to suggest that even the most recent Σ DDT and Σ PCBs residues had undergone extensive ageing under terrestrial conditions before their transport and deposition onto recent sediments, rather than long-range transport and/or secondary sources inputs. This pattern is consistent with the marked $\delta^{13}\text{C}$ terrigenous (allochthonous) fluvial signal in the sedimentary OC (Tesi et al., 2013), and seems to suggest that the most active transport pathway of Σ DDT and Σ PCBs is the Po River draining previously contaminated soils from its drainage basin and slowly releasing contaminants in the North Western Adriatic Sea (Lopes da Rocha et al., 2017).

4.4 Ecological Risk Assessment

Our data suggests that the presence of PAHs, DDTs and PCBs in sediments from the Adriatic Sea pose limited risk of toxicity to marine organisms. An exception is the

presence of dibenzo[a,h]anthracene (DahA) in levels that exceed TEL, which represents the concentration below which adverse effects to marine organisms are not expected to occur frequently. Regarding the mean-SQGs, our data revealed that both m-ERM and m-PEL were below 0.1, indicating that low or no adverse biological effect is expected (Long, 1998).

5. Conclusions

PAHs, PCBs and DDTs were investigated in sediment cores from the North Western Adriatic Sea and selected deep-sea areas from the South-Western Adriatic Margin (SWAM). To the best of our knowledge, this is the first study on their historical deposition in the SWAM. The main findings of this research can be summarized as follows:

- a) Concentrations of PCBs and DDTs present a decreasing trend in sediment cores from the Western Adriatic Sea after the 1980s due to international restrictions and national regulations, and their deposition matched their historical use in Italy in agreement with consumption and accumulation patterns detected in other regions and countries of the world;
- b) The vertical profiles of PAHs seem to reflect the shifts in contamination sources along the sediment cores, which is ultimately related to historical energy production and consumption in Italy;
- c) Sedimentary PAHs in the western Adriatic Sea are a mixture of combustion related emissions among which LMW, more susceptible to degradation processes, represent a minor fraction of the detected compounds. PAHs related to emissions from coal or biomass combustion show higher abundances in the bottom of the sediment cores (up to the ~1940s), while the abundance of PAHs

associated with coal burning and vehicle emissions increased from the mid- (~1945) to the top-sections (after 1980) of the sediment cores;

- d) The Po River prodelta is the area of the Western Adriatic Sea showing the highest concentrations of PAHs, PCBs and DDTs and an unlike decline have been recorded in the 21st century likely because the contaminant residues had undergone ageing before their transport and deposition onto the North Western sea floor.

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Table 1. Mean, standard deviation (SD), minimum and maximum values for fine sediments (silt and clay, %), organic carbon (C_{org} , %), and contaminant annual fluxes ($ng\ cm^{-2}\ y^{-1}$) for the sediment cores from the Bari canyon (station 1), sediment Drift (station 2), and Po River prodelta (station 9).

		Min.	Max.	Mean	SD
Station 1	Silt + clay	93.3	99.1	96.9	1.3
	Corg	0.4	0.6	0.5	0.06
	PAHs	1.8	4.9	3.3	0.9
	PCBs	0.0	0.15	0.03	0.02
	DDTs	0.0	0.14	0.04	0.04
Station 2	Silt + clay	96.2	98.7	97.4	0.7
	Corg	0.3	0.6	0.45	0.08
	PAHs	0.9	3.3	1.8	0.55
	PCBs	0.0	0.1	0.02	0.03
	DDTs	0.0	0.05	0.02	0.02
Station 9	Silt + clay	90	99.6	98.5	1.0
	Corg	0.6	1.0	0.9	0.09
	PAHs	90	228	151	30
	PCBs	0.4	2.2	1	0.32
	DDTs	0.02	1.1	0.42	0.18

Table 2. Comparison of total PAH, PCB and DDT concentrations (in ng g⁻¹ dry weight)

Study area	Time interval	ΣPAHs	ΣPCBs	ΣDDTs	References
Po river prodelta	1920-2014	193-533 ^a	0.9-5.2 ^g	0.1-2.5 ^m	This study
Off Bari Canyon	1880-2014	24-74 ^a	0.1-2.1 ^g	<DL-1.4 ^m	This study
Dauno seamount	1880-2014	11-49 ^a	<DL-2.1 ^g	<DL-0.7 ^m	This study
Po river prodelta	1966-1990	152-383 ^b	80.0 ^h	<1.0 ⁿ	Caricchia et al. (1993)
Po river prodelta	1974-1990	102-346 ^c	-	-	Guzzella and Paolis (1994)
Po river prodelta	1939-2012	-	0.7-3.0 ^g	-	Combi et al. (2016)
Gondola slide (southern Adriatic)	1894-2007	-	<DL-0.2 ^g	-	Combi et al. (2016)
Northwest coast of Spain	1950-2011	49.6-2489 ^d	-	-	Pérez-Fernández et al. (2016)
İzmit Bay, Turkey	1954-2006	258-1632 ^e	5.4-29 ⁱ	-	Giuliani et al. (2017)
East China Sea	1860-2009	18.8-96.5 ^a	0.1-2.5 ^j	<DL-1.5 ^o	Cai et al. (2016)
Gulf of Thailand	1940-2004	10-120 ^f	<DL-2.3 ^k	-	Boonyatumanond et al. (2007)
Western Barents Sea	1850-2000	35.3-132 ^b	0.7-3.5 ^g	-	Zaborska et al. (2011)
Admiralty Bay, Antarctica	1861-2006	<DL-454.9 ^a	-	-	Martins et al. (2010)
	1931-2006	-	<DL-11.9 ^l	-	Combi et al. (2017)

^a: Σ₁₆PAHs; ^b: Σ₁₂PAHs; ^c: Σ₁₀PAHs; ^d: Σ₃₅PAHs; ^e: Σ₁₅PAHs; ^f: Σ₁₈PAHs

^g: Σ₅PCBs; ^h: not informed; ⁱ: Σ₁₂₇PCBs; ^j: Σ₂₀PCBs; ^k: Σ₂₄PCBs; ^l: Σ₇PCBs

^m: Σp,p'-DDT, p,p'-DDD, p,p'-DDE; ⁿ: DDE; ^o: Σp,p'-DDT, p,p'-DDD, p,p'-DDE, o,p'-DDT, o,p'-DDD, o,p'-DDE

DL: detection limit

in sediment cores from other locations.

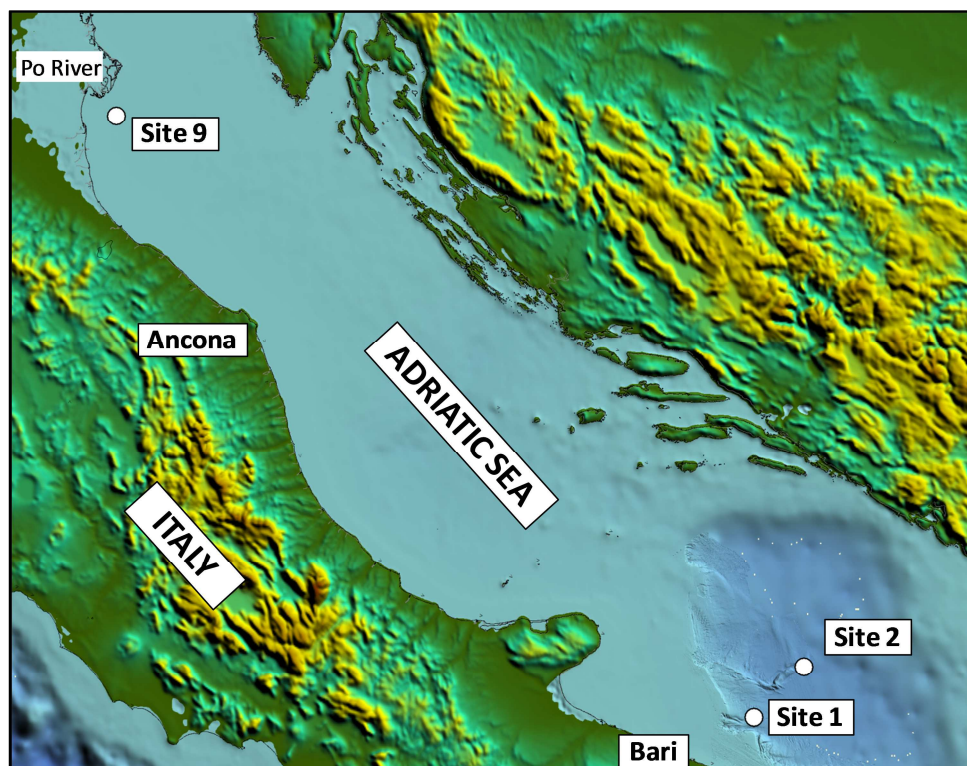


Figure 1. Map of the study area showing the sampling stations in the Adriatic Sea.

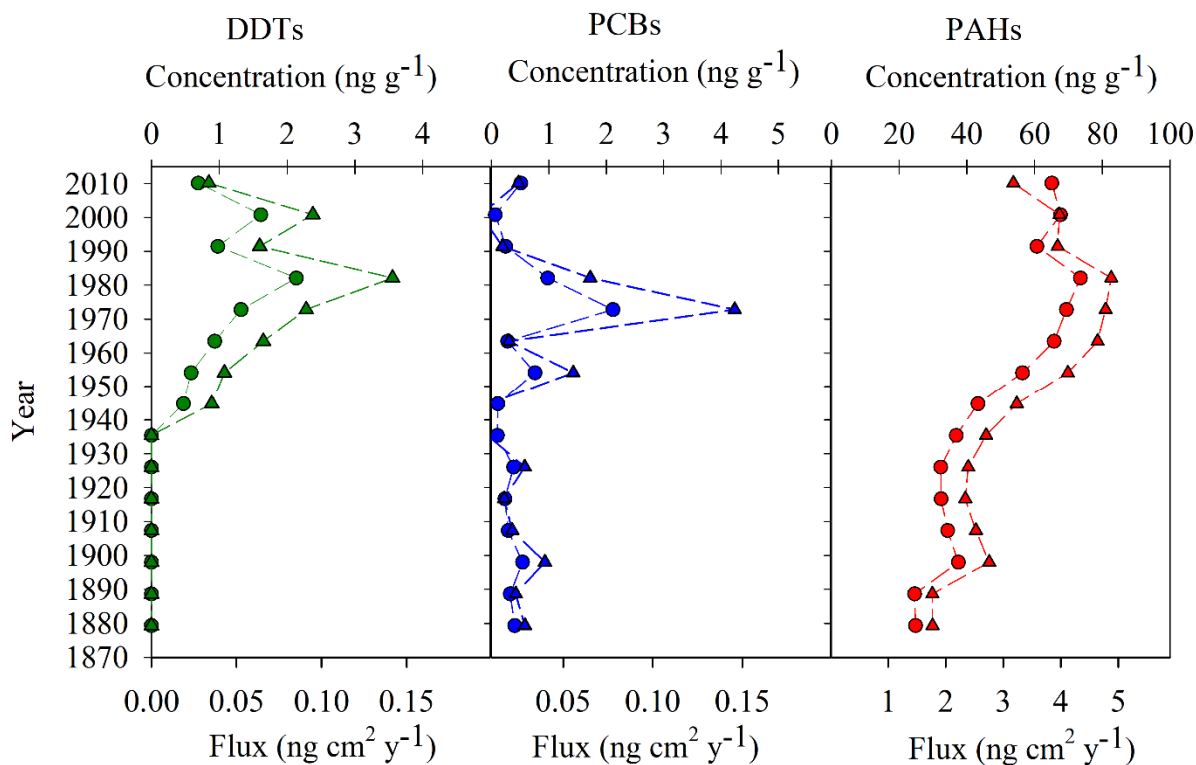


Figure 2. Historical records of PAHs, DDTs and PCBs in sediment cores taken off the Bari canyon (station 1) on deep South-Western Adriatic Margin (SWAM). Circles represent contaminant concentrations (ng g⁻¹) and triangles represent contaminant fluxes (ng cm² y⁻¹).

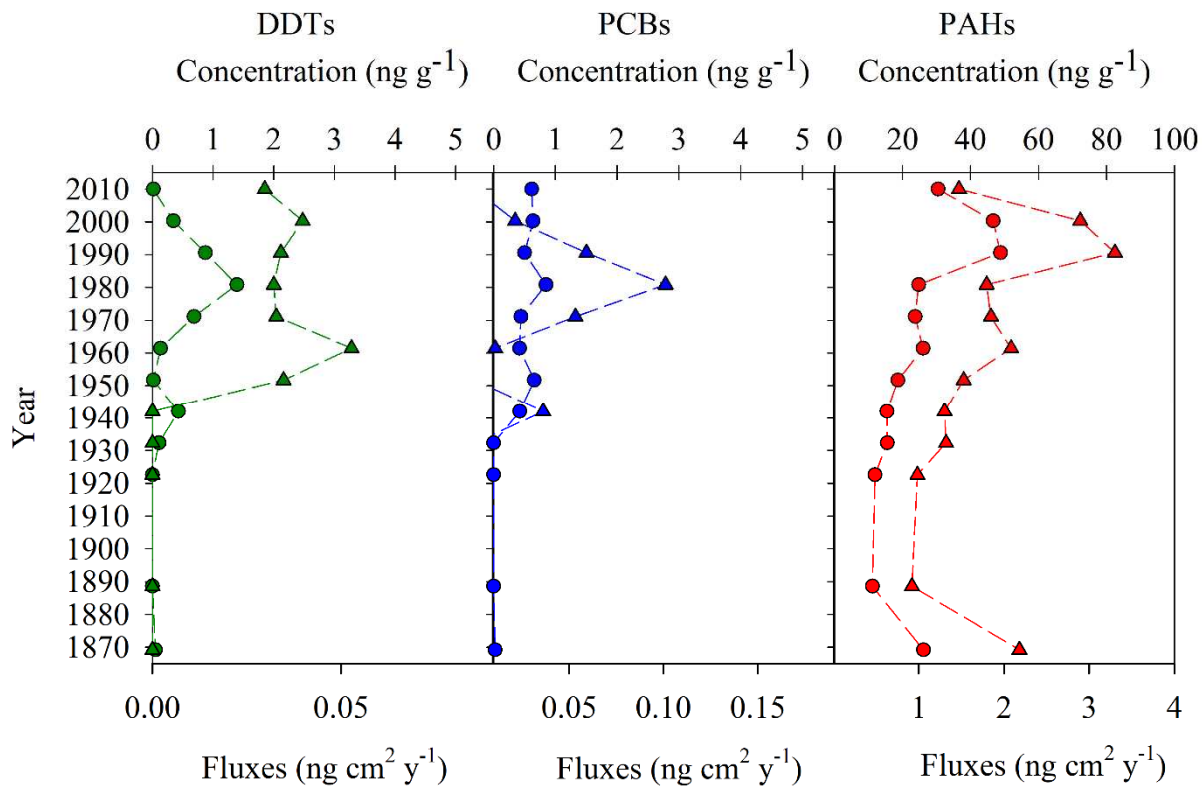


Figure 3. Historical records of PAHs, DDTs and PCBs in sediment cores taken in the Sediment Drift (station 2) on deep South-Western Adriatic Margin (SWAM). Circles represent contaminant concentrations (ng g⁻¹) and triangles represent contaminant fluxes (ng cm² y⁻¹).

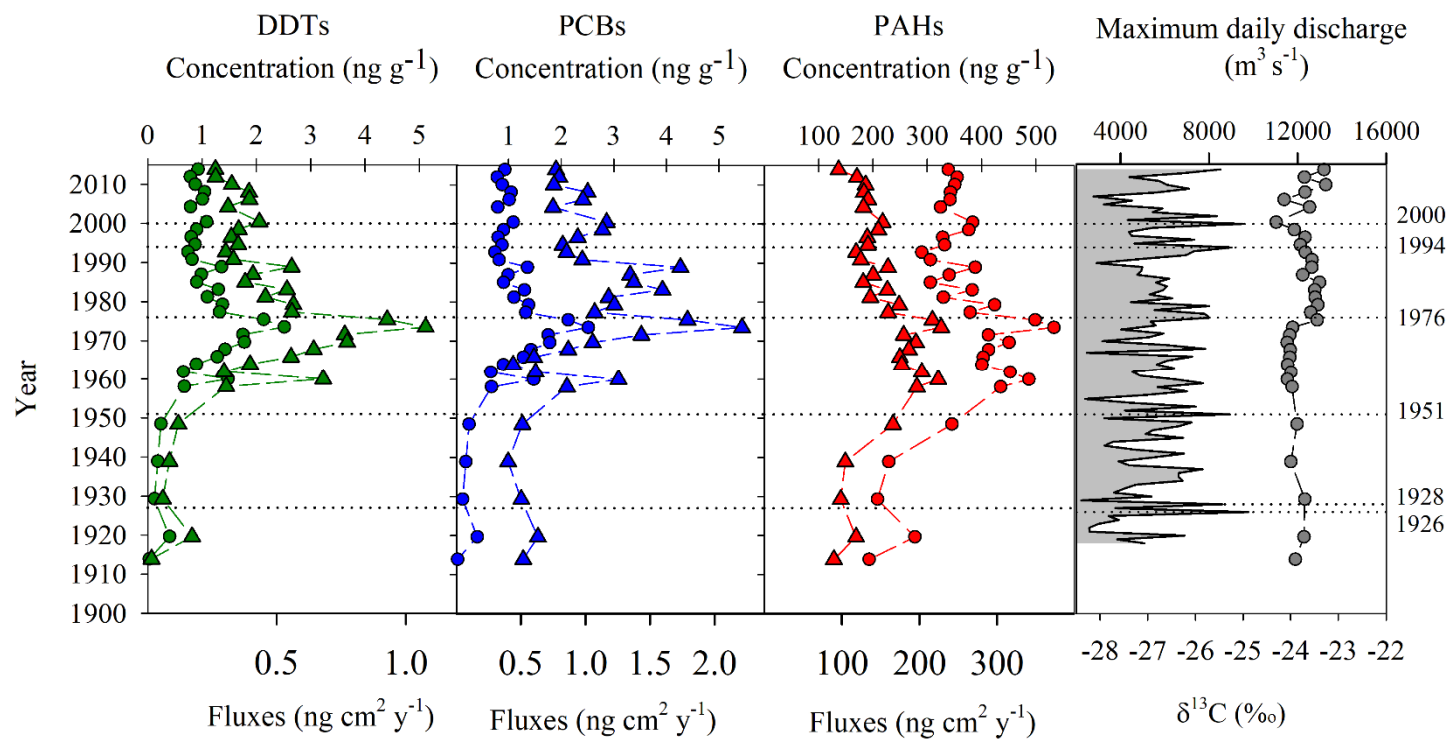


Figure 4. Historical records of PAHs, DDTs and PCBs, $\delta^{13}\text{C}$ variation (‰) in the Po River prodelta (station 9); chronological reconstruction of maximum daily discharges with marked major flood events ($> 8,000 \text{ m}^3 \text{ s}^{-1}$). Circles represent contaminant concentrations (ng g^{-1}) and triangles represent contaminant fluxes ($\text{ng cm}^2 \text{ y}^{-1}$).

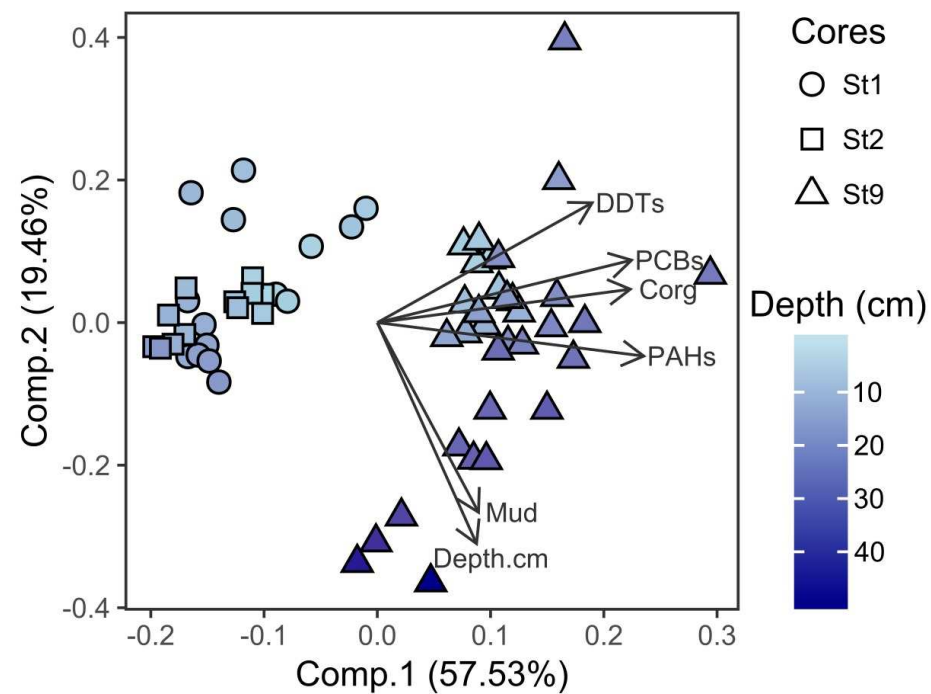


Figure 5. Principal component analysis (PCA) plot of contaminant (Σ PAHs, Σ PCBs, and Σ DDTs) and sediment characteristics (mud (i.e. silt + clay) and C_{org}) data.

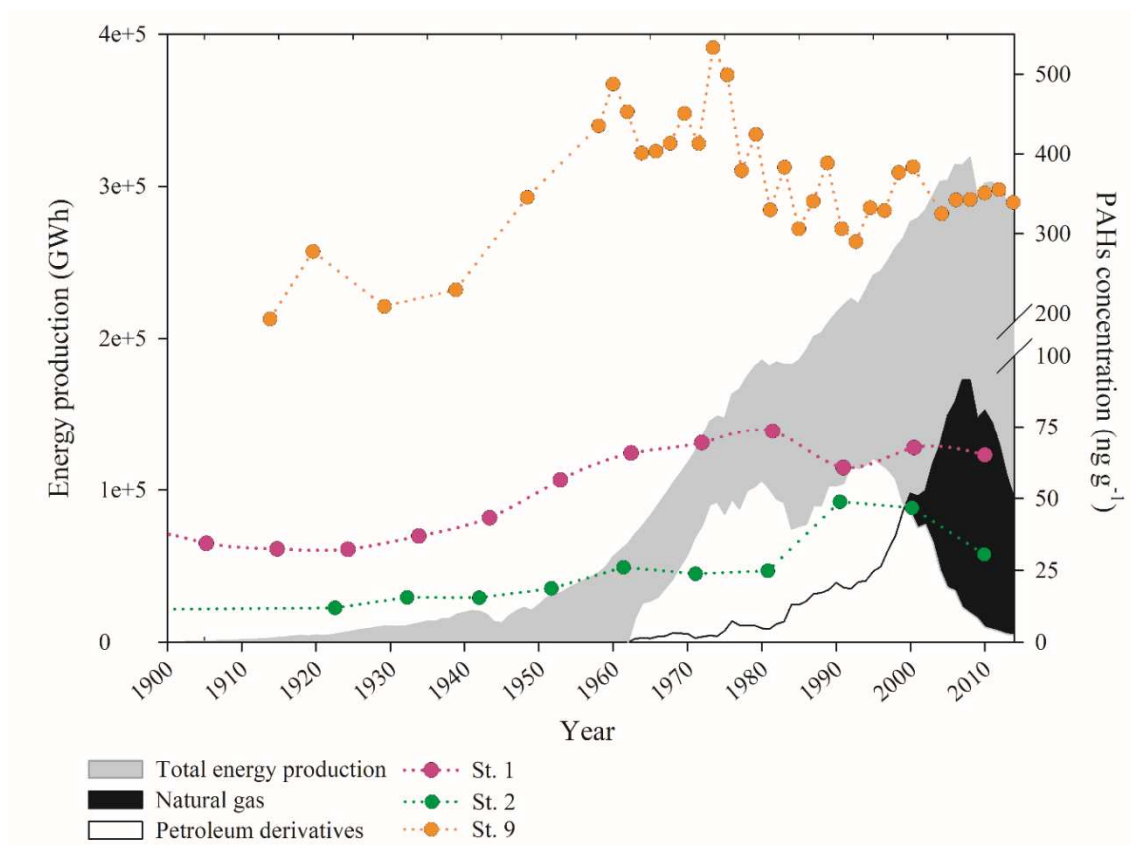


Figure 6. Historical variation of PAHs concentrations in the sediment cores from the Adriatic Sea (ng g⁻¹) and energy production (GWh) in Italy.

Highlights:

- Unprecedented data of historical deposition of contaminants in the SWAM were assessed
- The first use of DDT in Italy followed the typhus epidemics during the II World War
- Concentrations of PCB and DDT decreased after 1980 due to international restrictions
- Historical variation of PAHs seem to follow shifts in energy production in Italy
- The deep Adriatic basin represents as an important repository for contaminants

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: