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

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

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17

18 **Abstract**

19 The sources and depositional history of polycyclic aromatic hydrocarbons (PAHs) and
20 organochlorine compounds (OCs) over the last century were investigated in sediment
21 cores from the North Adriatic Sea (Po River prodelta) and the South-Western Adriatic
22 Margin (SWAM). Contaminant concentrations were higher in the Po River prodelta.
23 $\sum_{16}\text{PAHs}$ ranged from 193 to 533 ng g⁻¹, $\sum_5\text{PCBs}$ ranged from 0.9 to 5.2 ng g⁻¹ and
24 $\sum\text{DDTs}$ (*p,p'*-DDD + *p,p'*-DDE) ranged from 0.1 to 2.5 ng g⁻¹. In the SWAM, $\sum\text{PAHs}$
25 ranged from 11 to 74 ng g⁻¹ while $\sum\text{PCB}$ and $\sum\text{DDT}$ concentrations were close to the
26 MQL. Accordingly, contaminant fluxes were much higher in the northern (mean values
27 of 152 ± 31 ng cm² y⁻¹ and 0.70 ± 0.35 ng cm² y⁻¹ for PAHs and OCs, respectively) than
28 in the southern Adriatic (2.62 ± 0.9 ng cm² y⁻¹ and 0.03 ± 0.02 ng cm² y⁻¹ for PAHs and
29 OCs, respectively). The historical deposition of PAHs seemed to be influenced by the
30 historical socioeconomic development and by changes in the composition of fossil fuel
31 consumption (from petroleum derivatives to natural gas) in Italy from the end of the 19th
32 century to the present. Similarly, vertical variations in DDT concentrations matched its
33 historical use and consumption in Italy, which started around in the mid- late 1940s to
34 fight typhus during the II World War. Contaminant concentrations detected in
35 sediments does not seem to pose ecotoxicological risk for marine organisms in the
36 Adriatic Sea.

37

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

40 1. Introduction

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

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

58 Due to their long-range atmospheric transport potential and harmful effects on man and
59 wildlife, regulatory efforts and international agreements have been made in past decades
60 in order to reduce future environmental burdens (Breivik et al., 2004; Vallack et al.,
61 1998). At global scale, POPs are regulated by the Stockholm Convention under which
62 the signatory countries are legally required to eliminate the production, use, and
63 emissions of POPs, with the ultimate goal of reducing human and ecosystem exposure
64 (Holoubek and Klánová, 2008; Nizzetto et al., 2010). Parallel efforts have been made at

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

70 These regulatory actions have led to the reduction or elimination of major primary
71 sources associated with the production and use of POPs, followed by a gradual decline
72 on environmental levels of these contaminants over time, especially after the 1980's
73 (Franců et al., 2009; Smith et al., 2009; Combi et al., 2016; Neves et al., 2018).
74 However, there are still ongoing primary releases from diffuse sources that are difficult
75 to target for reduction or elimination, such as volatilization from old stockpiles or from
76 old equipment that is still in use (Breivik et al., 2002; Nizzetto et al., 2010).
77 Additionally, these compounds are highly persistent in the environment and continue to
78 be found in different environmental media, and their current levels are not expected to
79 decrease significantly within the next decades (Breivik et al., 2007). Evidence of this
80 unlike decline or even an increase in DDTs and/or PCBs levels has been recently
81 observed in the Arctic Fjords, glaciers and snow (Bartlett et al., 2019; Pouch et al.,
82 2017; Garmash et al., 2013), in the Baltic Sea (Sobek et al., 2015), the Gulf of Thailand
83 (Kwan et al., 2014), and the Korea Strait (Guerra et al., 2019), due to unintentional
84 sources released from by-products of manufacturing (e.g. paint pigments; Hu and
85 Hornbuckle, 2010), from thermal sources (e.g. steel making processes; Baek et al, 2010)
86 and e-waste (Breivik et al., 2016), or from melting glaciers and the cryosphere affected
87 by climate change-related processes (Sun et al., 2018; Pavlova et al., 2015). Therefore,
88 it is essential to understand the temporal trends of contaminant loads into the

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

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

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

108

109 **2. Material and methods**

110

111 *2.1. Study area and sediment cores sampling*

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

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

134 In the context of the task 'ADREX: Adriatic and Ionian Seas Experiment' within the
135 PERSEUS project, sediments were collected in the western Adriatic Sea in October
136 2014 on board the O/V OGS Explora at the following key stations: the Po River

137 prodelta (station 9; ~27 m water depth); off the Bari Canyon (station 1; ~709 m water
138 depth); and in a giant sediment drift (Foglini et al., 2016) in the centre of the South
139 Adriatic (station 2; ~1040 m water depth; Figure 1). Undisturbed sediment cores (length
140 ≤ 50 cm; diameter: 10 cm) were retrieved using a cylindrical box-corer or the gravity
141 sediment corer SW104, and sectioned onboard at 1-2 cm intervals. Sediments were
142 placed into pre-cleaned glass containers and stored at -20 °C until processing and
143 analysis.

144

145 2.2. Sediment characteristics

146 Sediment samples were weighed, oven-dried at 55 °C, and then re-weighed to determine
147 water content. Porosity (ϕ) was calculated from the loss of water between wet and dry
148 sediments according to equations suggested by Berner (1971), assuming a sediment
149 density of 2.6 g cm^{-3} and a water density of 1.034 g cm^{-3} . Grain size was determined
150 after a pre-treatment with H_2O_2 and wet sieving at 63 μm to separate sands from fine
151 fractions. Total carbon (TC) and total nitrogen (TN) content were determined by
152 elemental analysis (EA) of combusted aliquots with a Fison CHNS-O Analyzer EA
153 1108, and organic carbon (C_{org}) was measured on decarbonated samples (1 M HCl).
154 Stable isotopic analyses of organic C ($\delta^{13}\text{C}$) were carried out on the same samples using
155 a FINNIGAN Delta Plus mass spectrometer directly coupled to the FISIONS NA2000
156 EA by means of a CONFLO interface for continuous flow measurements.

157

158 2.4. Extraction and clean-up

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

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

173

174 *2.5. Instrumental analysis*

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

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

196

197 2.6. *Quality assurance and quality control (QA/QC)*

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

204

205 2.7. *Data analysis*

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

211

212 *2.8. Sediment dating and fluxes*

213 Since information on sediment accumulation rates (SARs) have been extensively
 214 assessed in the northern Adriatic Sea, different datasets were combined based on
 215 triangle-based linear interpolation (Frignani et al., 2005; Palinkas and Nittrouer, 2007;
 216 Tesi et al., 2013) to estimate the SARs for the sediment core from the Po River prodelta
 217 (station 9). Conversely, information on strata chronologies in the deep Adriatic is rather
 218 scarce. Thus, sediment cores from the southern Adriatic (Stations 1 and 2) were
 219 measured for ^{210}Pb activities. Alpha counting of daughter isotope ^{210}Po , considered in
 220 secular equilibrium with its grandparent Ra^{226} , was used for ^{210}Pb analyses. Estimated
 221 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)
 222 were used to estimate the date for each section of the sediment cores as follows:

$$223 \quad \text{Estimated date [anno Domini (A.D.)]} = a - \left(\frac{b}{c} \right)$$

224 where a is the year in which the core was collected, b is the depth of the section in the
 225 core and c is the SAR of each core.

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

$$227 \quad C_i \times r \times \rho_i$$

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

231

232 *2.9. Ecological Risk Assessment*

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

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

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

246

247 **3. Results**

248 *3.1 Sediment characteristics*

249 Sediment cores were collected in areas where preferential accumulation of fine-grained
250 sediments was previously reported (Frignani et al., 2005; Tesi et al., 2007).
251 Accordingly, fine sediments (i.e. silt + clay) were detected in percentages above 90% in
252 the analyzed samples. Vertical distribution of fine sediments was relatively constant in
253 the sediment cores, with mean values of $96.9 \pm 1.3\%$ at station 1 (off the Bari canyon),
254 $97.4 \pm 0.7\%$ at station 2 (sediment drift), and $98.5 \pm 1\%$ at station 9 (Po River prodelta,

255 Table 1). In general, organic carbon (C_{org}) was also constant (mean values of $0.5 \pm$
256 0.06% , $0.45 \pm 0.08\%$, and $0.9 \pm 0.09\%$ at station 1, station 2, and station 9,
257 respectively), with a slight increase from the bottom to the top sections of the sediment
258 cores.

259

260 3.2 Organochlorine compounds

261 The highest concentrations of organochlorine compounds (OCs) were detected in the Po
262 River prodelta. Total PCBs ($\sum_5\text{PCBs}$) ranged from 0.9 to 5.2 ng g^{-1} ($2.4 \pm 0.8 \text{ ng g}^{-1}$),
263 with predominance of congeners PCB 138 and PCB 180, which accounted for 45% and
264 20% of total PCBs, respectively. $\sum\text{DDTs}$ (p,p' -DDD + p,p' -DDE) ranged from 0.1 to
265 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
266 p,p' -DDT under aerobic conditions, was the prevalent compound corresponding to
267 ~70% of total DDTs.

268 In the deep southern Adriatic, OCs levels were close to the MQL (0.01 to 0.06 ng g^{-1} for
269 PCBs and 0.04 to 0.3 ng g^{-1} for DDTs) and were detected in roughly half of the
270 samples. Only PCB congeners 138 and 180 were detected in measurable amounts and
271 their sum ranged between 0.1 and 2.1 ng g^{-1} ($0.5 \pm 0.3 \text{ ng g}^{-1}$), and between $<\text{DL}$ and 1.4
272 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),
273 respectively. The $\sum\text{DDTs}$ ranged from $<\text{DL}$ to 2.1 ng g^{-1} ($0.6 \pm 0.6 \text{ ng g}^{-1}$) at station 1
274 and from $<\text{DL}$ to 0.7 ng g^{-1} ($0.3 \pm 0.3 \text{ ng g}^{-1}$) at station 2.

275

276 3.3 PAHs

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

279 74 ng g⁻¹ (48.3 ± 16 ng g⁻¹) in sediment core 1 (off the Bari canyon; Figure 2); from 11
280 to 49 ng g⁻¹ (25 ± 9 ng g⁻¹) in sediment core 2 (sediment drift; Figure 3); and from 193
281 to 533 ng g⁻¹ (mean ± SD of 363 ± 59 ng g⁻¹) in sediment core 9 (Po River prodelta;
282 Figure 4).

283 The relative abundance of individual PAHs was calculated as their concentrations in
284 relation to the average \sum_{16} PAHs concentration over the entire depth of sediment cores
285 to evaluate sedimentary PAH compositions and potential spatial differences (Liu et al.,
286 2012). PAHs in sediments of the western Adriatic Sea exhibited a quite uniform
287 distribution, with a predominance of high-molecular weight PAHs (HMW: 4-6 rings).
288 From these, 5- and 6-ring PAHs (BbF, BkF, BaP, IcdP, DahA, and BghiP) accounted
289 for 50 to 65% of total PAHs, while 4-ring PAHs (Fl, Py, BaA, and Chr) accounted for
290 20 to 33%. The presence of low-molecular weight PAHs (LMW: Na, Acy, Ace, Flo,
291 Phe, and An) PAHs was somewhat higher in the sediment taken in the sediment drift
292 (station 2; ~30%) in comparison to sediment cores taken off the Bari canyon (station 1;
293 15%) and in the Po River prodelta (station 9; 13%). The ratio between LMW and HMW
294 PAHs ranged from 0.1 to 1.4 in the sediment cores.

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

302

303 *3.4 Fluxes and vertical distribution of OCs and PAHs*

304 Similarly to concentration data, annual fluxes of OCs were lower in the southern
305 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,
306 respectively) in comparison to the northern Adriatic (0.02 to 2.2 ng cm² y⁻¹; Table 1).
307 Annual fluxes and concentrations of OCs (\sum_5 PCBs and \sum DDTs) followed a similar
308 vertical pattern in the three sediment cores (Figures 2, 3, and 4). In general, OCs were
309 un-detectable or negligible before the 1940s, when they first occurred in sediments from
310 the western Adriatic, followed by an increasing trend up to the middle/late 1970s - early
311 1980s. This sediment stratum displayed the highest concentrations of \sum_5 PCBs (2.1 ng g⁻¹,
312 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,
313 and 2.5 ng g⁻¹ in stations 1, 2, and 9, respectively). After the 1980s, annual fluxes and
314 concentrations of OCs decreased upwards until recent sediments, where PCBs presented
315 concentrations of 0.5 ng g⁻¹, <LQ, and 2.7 ng g⁻¹ and DDT presented concentrations of
316 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),
317 and 9 (Po river prodelta), respectively.

318 PAHs presented the highest fluxes (152 ± 31 ng cm² y⁻¹) in the Po River prodelta
319 (station 9), followed by off the Bari canyon (station 1; 3.2 ± 0.9 ng cm² y⁻¹) and the
320 sediment drift (station 2; 1.8 ± 0.5 ng cm² y⁻¹). PAHs fluxes and concentrations
321 presented similar patterns along the sediment cores. The oldest sections of the sediment
322 cores (before 1940) displayed the lowest mean concentrations of \sum_{16} PAHs (32 ± 4 ng g⁻¹,
323 16 ± 4 ng g⁻¹, and 227 ± 26 ng g⁻¹ in, off the Bari canyon, the sediment drift and the
324 Po River prodelta (stations 1, 2, and 9, respectively). Afterwards, mean concentrations
325 of \sum_{16} PAHs increased to 62 ± 8 ng g⁻¹, 48 ± 1 ng g⁻¹, and 392 ± 32 ng g⁻¹ in sediment
326 cores off the Bari canyon (station 1), in the Sediment rift (station 2), and in the Po River
327 prodelta (station 9), respectively. Mean concentrations of \sum_{16} PAHs show a somewhat

328 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,
329 and $348 \pm 12 \text{ ng g}^{-1}$ in station 9.

330

331 *3.5 Ecological Risk Assessment*

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

340

341 **4. Discussion**

342

343 *4.1. Levels of OCs and PAHs in sediments*

344 Few studies have reported the temporal distribution of organic contaminants along the
345 Adriatic Sea. PAHs levels detected in the Po River prodelta in our study were slightly
346 higher when compared to those previously detected in the same area (102 to 346 ng g^{-1} ;
347 Guzzella and Paolis, 1994), whereas PCBs and DDTs concentrations were lower and/or
348 comparable to previous levels (Caricchia et al., 1993; Combi et al., 2016). Regarding
349 the deep southern Adriatic, such data are even scarcer and PCB levels in our study were
350 slightly higher than previously reported ($<DL-0.2 \text{ ng g}^{-1}$ for Σ_5 PCBs; Combi et al.,
351 2016).

352 PAH concentrations in our study were lower in comparison to those reported in
353 sediment cores from coastal areas subject to industrial activities such as the northwest
354 coast of Spain (Pérez-Fernández et al., 2016) and Izmit Bay, Turkey (Giuliani et al.,
355 2017). While PAH levels in the Po river prodelta were higher in comparison to less-
356 impacted and open sea areas (Table 2), concentrations in the southern Adriatic were
357 comparable to those detected in the continental shelf of the East China Sea (Cai et al.,
358 2016), the Gulf of Thailand (Boonyatumanond et al., 2007), and in remote areas such as
359 the Arctic (Zaborska et al., 2011) and Antarctica (Martins et al., 2010b). Overall, the
360 levels of OCs in our study were comparable to those detected in the East China Sea, the
361 Gulf of Thailand, and the Western Barents Sea (Boonyatumanond et al., 2007; Cai et
362 al., 2016; Zaborska et al., 2011) whilst PCBs were fairly below the maximum values
363 reported in Izmit Bay (Giuliani et al., 2017) and Antarctica (Combi et al., 2017).

364

365 *4.2 Source assessment*

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

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

377 and anthropogenic petroleum spillages (Magi et al., 2002; Readman et al., 2002).
378 Generally, pyrolytic sources are depleted in low-molecular weight PAHs (LMW: 2–3
379 rings) and enriched in high-molecular weight PAHs (HMW: 4–6 rings) leading to
380 LMW/HMW ratio < 1 (Merhaby et al., 2015; Jafarabadi et al., 2017). Thus, the ratios
381 between LMW and HMW PAHs reported in our study indicate the predominance of
382 pyrolytic sources in the western Adriatic Sea. Similarly, the diagnostic ratios $Fl/(Fl +$
383 $Py)$ and $IcdP/(IcdP + BghiP)$ indicated pyrolytic sources of PAHs related to biomass
384 combustion in the southern Adriatic (stations 1 and 2). A separated cluster can be
385 identified for the Po River prodelta (station 9; Figures S1 and S2 from Supplementary
386 Material) probably because, in addition to biomass combustion, petroleum combustion
387 also represented a source of PAHs in this sediment core.

388

389 *4.3 Historical records of PAHs, PCBs and DDTs in the Western Adriatic Sea*

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

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

402 Another factor influencing PCBs vertical patterns (Figures 2, 3, and 4) is related to the
403 production and use of these compounds worldwide. PCB peak concentrations coincide
404 with the beginning of the production of PCB by the Caffaro industry in northern Italy
405 (1935-1983; Panizza and Ricci, 2002), as well as with the predicted trends on PCB
406 consumption and emission in the country (Breivik et al., 2002, 2007; Combi et al.
407 2016).

408 Similarly, the historical deposition of DDTs in sediments from the western Adriatic Sea
409 matches its historical use and consumption in Italy. DDTs first appeared in detectable
410 concentrations in sediments in the mid- late 1940s following its first massive use to
411 fight a severe typhus epidemics affecting the civilians and military personnel in 1943-
412 1944 (Wheeler, 1946; Soper et al., 1947). After end of the II World War, DDT was
413 extensively used in indoor and outdoor treatment mainly in the Central and Southern
414 regions, major islands and North-eastern coastal areas, and continued into the mid-
415 1950s and even later in some hyperendemic areas (Majori, 2012) as evidenced by the
416 1960s subsurface peak in the Po River prodelta station. In the 1970s and 1980s,
417 agricultural use of DDT was banned in most developed countries including Italy, and
418 this is reflected in the decreasing historical deposition observed in the sediments from
419 the western Adriatic Sea (Figures 2, 3, and 4).

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

426 Historical deposition of PAHs showed a common trend in sediment cores from the Po
427 River prodelta (station 9), off the Bari canyon and at the sediment drift (stations 1 and
428 2). The lowest concentrations were reported in the bottom strata (end of the 1880s –
429 beginning of the 1900s). This finding is consistent with the relatively low consumption
430 and production of energy in Italy from the end of the 1800 until the Second World War
431 (Malanima, 2011). In comparison to periods after ~1940, LMW PAHs were relatively
432 more abundant in the oldest sections of the sediment cores (Figure S3 from
433 Supplementary Material). These PAHs are usually generated by moderate temperature
434 combustion processes such as biomass and coal burning in homes and small factories
435 (Cai et al., 2016; Yunker et al., 2002). The predominance of LMW PAHs is particularly
436 evident in the sediment core from the sediment drift (station 2), that dates back to the
437 1870's when Italy was almost completely dependent on biomass burning as a source of
438 energy and firewood accounted for half of the total energy consumption (Malanima,
439 2006).

440 Afterwards, concentrations increased from the lower strata to the middle sections of
441 sediment cores (1960s – 1990s). Σ PAH, Σ PCB and Σ DDT displayed a synchronous
442 deposition with maximum peak values recorded in the mid-1970s in the Po prodelta
443 station, and at the beginning of the 1980s for Σ DDT and Σ PAH in the South-Western
444 Adriatic Margin (SWAM) stations. This period corresponds to the modern stage of
445 economic and industrial development in Italy, the so-called "Economic Miracle"
446 (~1945-1970), marked by mass motorization, switch from coal to oil, and industrial
447 development (Romano et al., 2013). In this section, there is a change in the relative
448 abundances of low- and high-molecular weight PAHs: whereas the former decreases,
449 the latter increases until the middle of the 20th century (Figure S3 from Supplementary
450 Material). Since HMW PAHs are usually generated during high-temperature

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

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

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

476 1970's, a subsurface peak in Σ PAH , and to a lesser extent an increase in OCs
477 concentrations, can be identified after a Po River's flood occurring in November 2000.
478 This event represents the largest flood occurring in the previous century and recorded a
479 mean daily maximum water discharge above $9,000 \text{ m}^3\text{s}^{-1}$ as well as the longest duration
480 of high river discharge ($> 4,000 \text{ m}^3\text{s}^{-1}$) (Tesi et al., 2008). The signature of this flood
481 event is clearly marked by the concurrent heaviest $\delta^{13}\text{C}$ signal, indicating the
482 predominance of riverine sources within the same period (Miserocchi et al.; 2007).
483 Large floods can mobilize upstream contaminants sources, resulting in inputs of
484 contaminated sediments, and thus affect pollutants distribution (Mourier et al., 2014).
485 The OCs concentration reduction over time observed from the 1980s to the mid-late
486 1990s levelled off in the last two decades in the Po River prodelta, and concentrations
487 of Σ DDT and Σ PCBs appear to be at or near a steady-state condition in the XXI century.
488 The presence of DDD and DDE isomers, but not DDT, and more highly chlorinated
489 PCBs (PCB 138 and PCB 180) seems to suggest that even the most recent Σ DDT and
490 Σ PCBs residues had undergone extensive ageing under terrestrial conditions before their
491 transport and deposition onto recent sediments, rather than long-range transport and/or
492 secondary sources inputs. This pattern is consistent with the marked $d^{13}\text{C}$ terrigenous
493 (allochthonous) fluvial signal in the sedimentary OC (Tesi et al., 2013), and seems to
494 suggest that the most active transport pathway of Σ DDT and Σ PCBs is the Po River
495 draining previously contaminated soils from its drainage basin and slowly releasing
496 contaminants in the North Western Adriatic Sea (Lopes da Rocha et al., 2017).

497

498 *4.4 Ecological Risk Assessment*

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

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

506

507 **5. Conclusions**

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

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

526 associated with coal burning and vehicle emissions increased from the mid-
527 (~1945) to the top-sections (after 1980) of the sediment cores;

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

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541

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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	Σ PAHs	Σ PCBs	Σ DDTs	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)

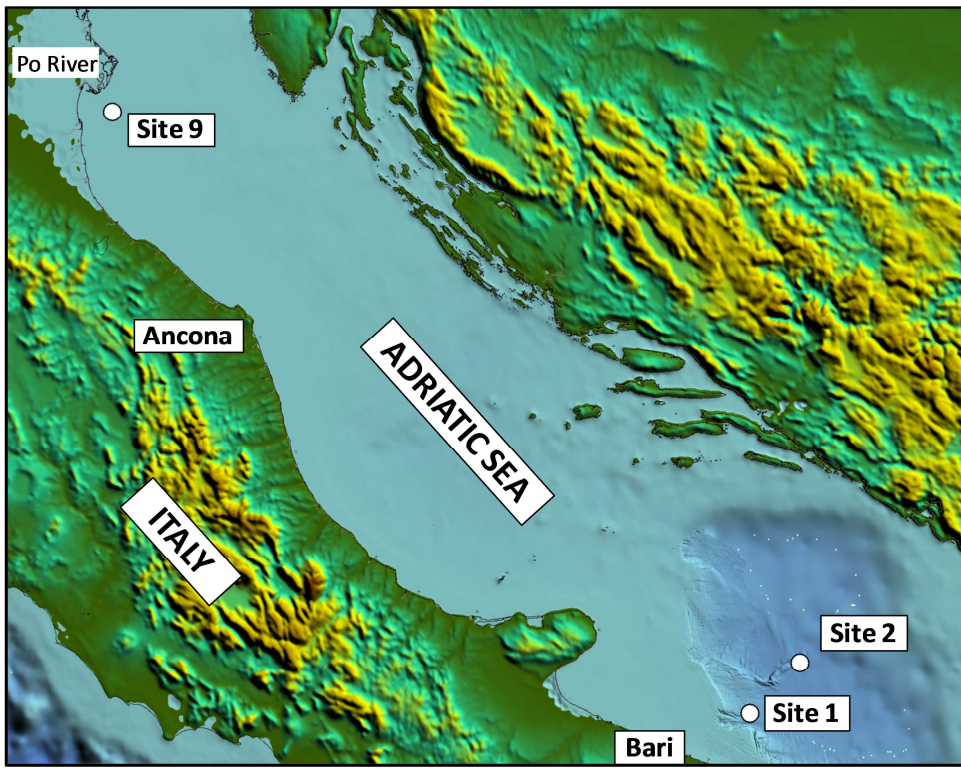
^a: Σ_{16} PAHs; ^b: Σ_{12} PAHs; ^c: Σ_{10} PAHs; ^d: Σ_{35} PAHs; ^e: Σ_{15} PAHs; ^f: Σ_{18} PAHs

^g: Σ_5 PCBs; ^h: not informed; ⁱ: Σ_{127} PCBs; ^j: Σ_{20} PCBs; ^k: Σ_{24} PCBs; ^l: Σ_7 PCBs

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

DL: detection limit

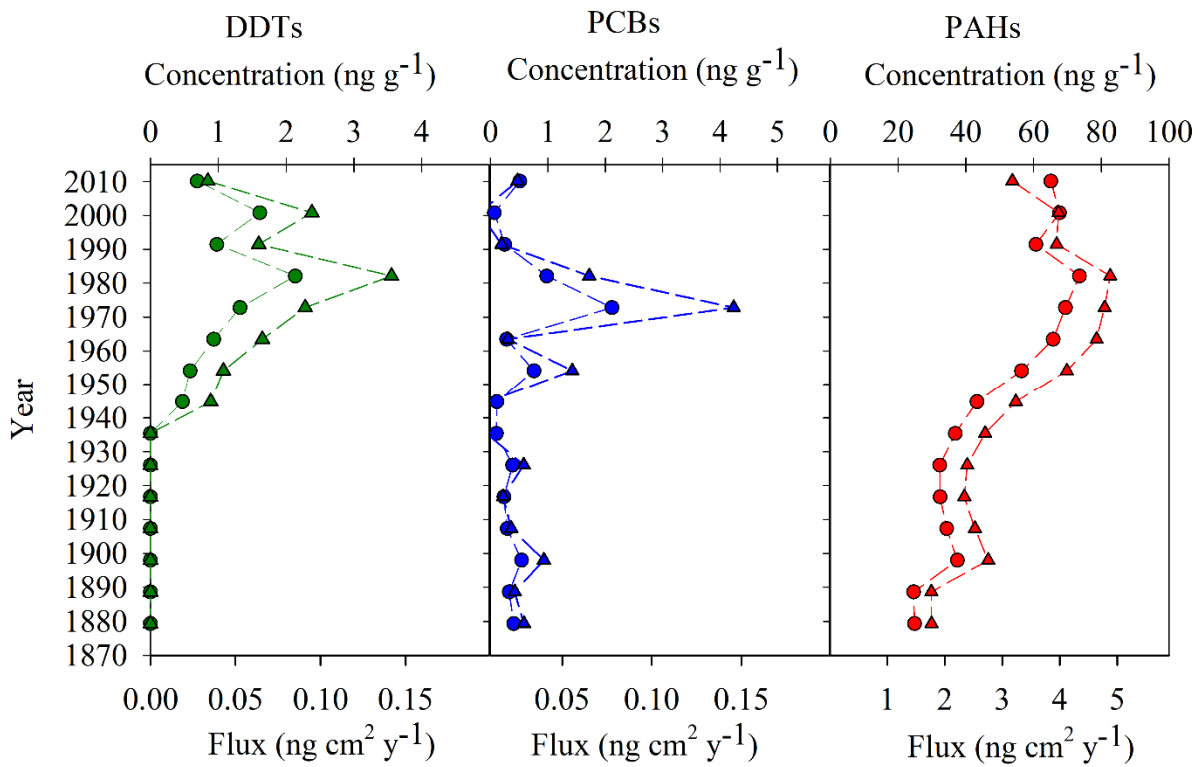
in sediment cores from other locations.



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

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

8

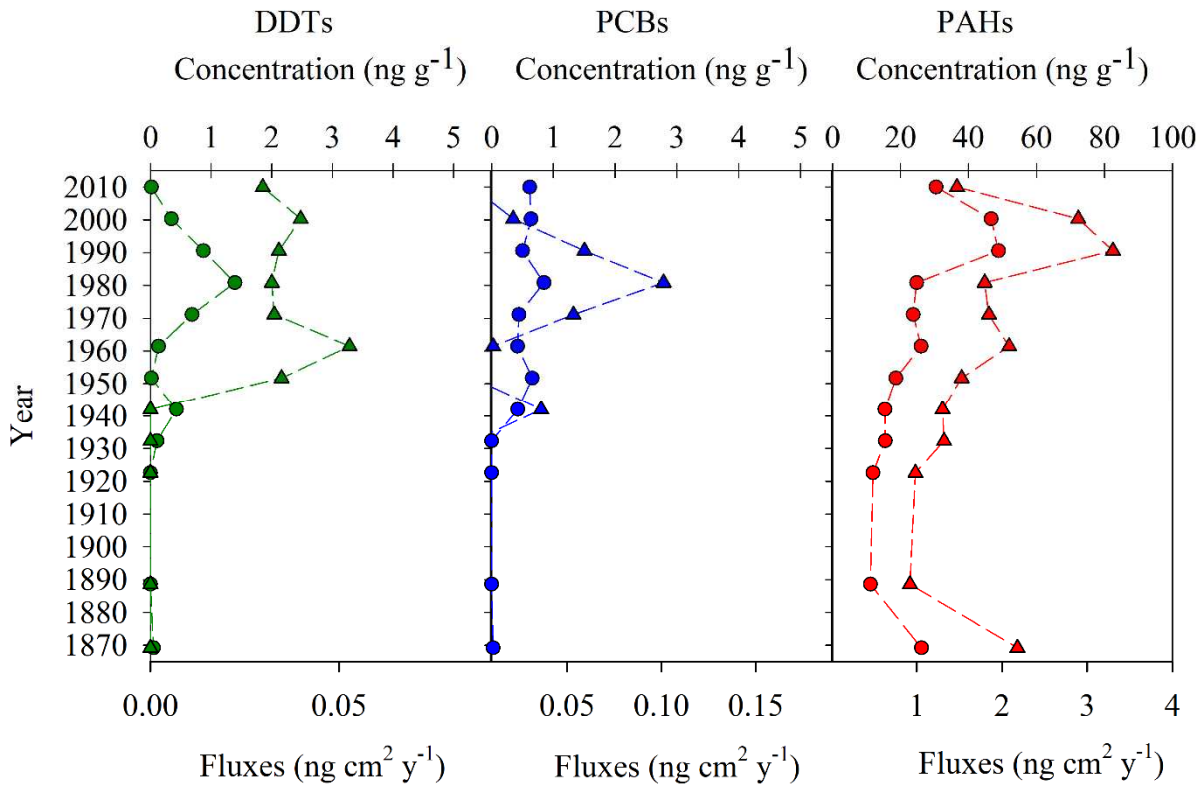


Figure 3. Historical records of PAHs, DDTs and PCBs in sediment cores taken in the Sediment Drift (station 2) on deep South-Western Adriatic Margin (SWAM). Circles represent contaminant concentrations (ng g⁻¹) and triangles represent contaminant fluxes (ng cm² y⁻¹).

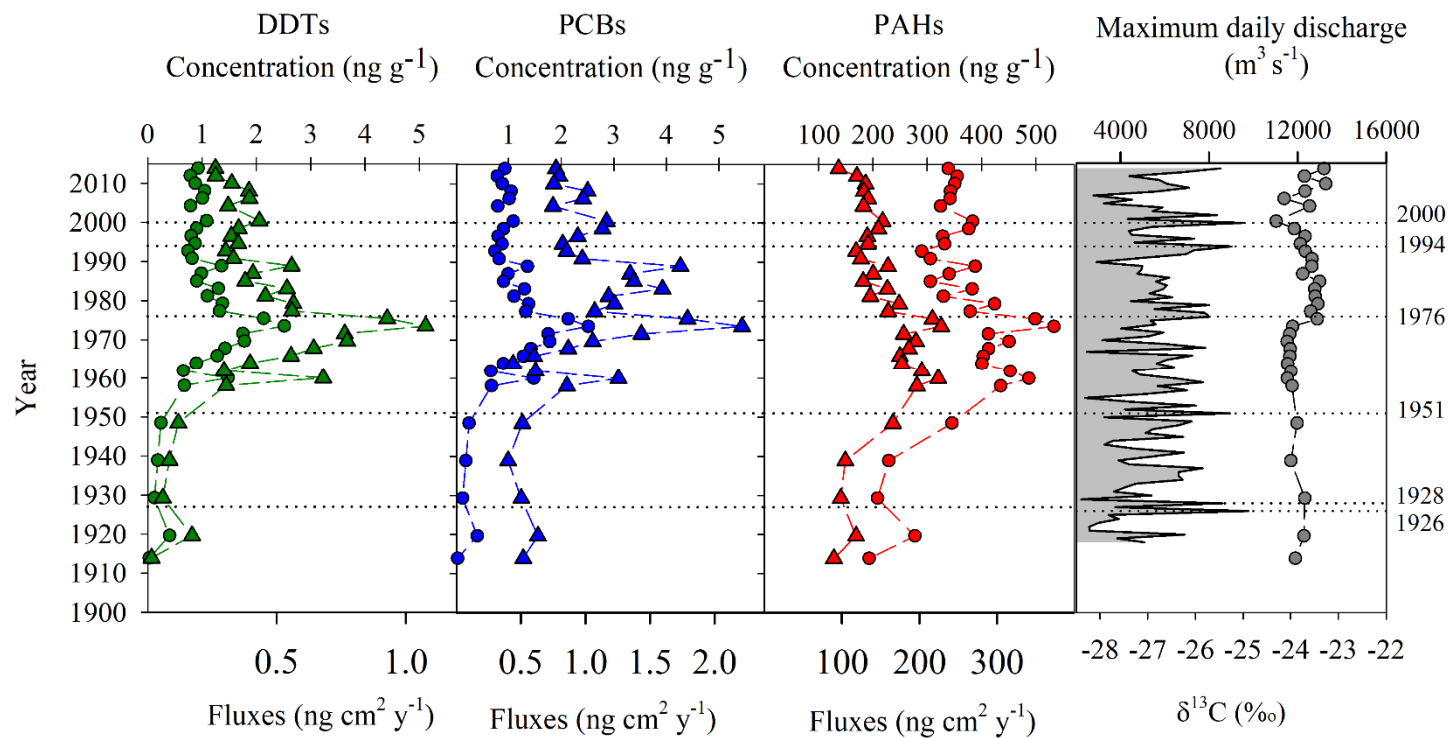


Figure 4. Historical records of PAHs, DDTs and PCBs, $\delta^{13}\text{C}$ variation (‰) in the Po River prodelta (station 9); chronological reconstruction of maximum daily discharges with marked major flood events ($> 8,000 \text{ m}^3 \text{ s}^{-1}$). Circles represent contaminant concentrations (ng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

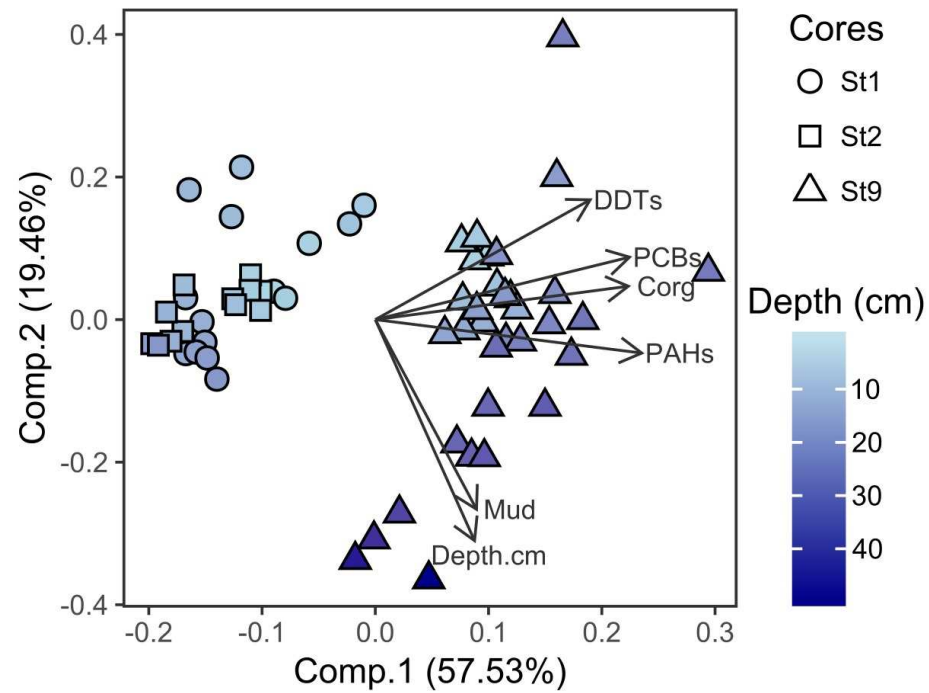


Figure 5. Principal component analysis (PCA) plot of contaminant (Σ PAHs, Σ PCBs, and Σ DDTs) and sediment characteristics (mud (i.e. silt + clay) and C_{org}) data.

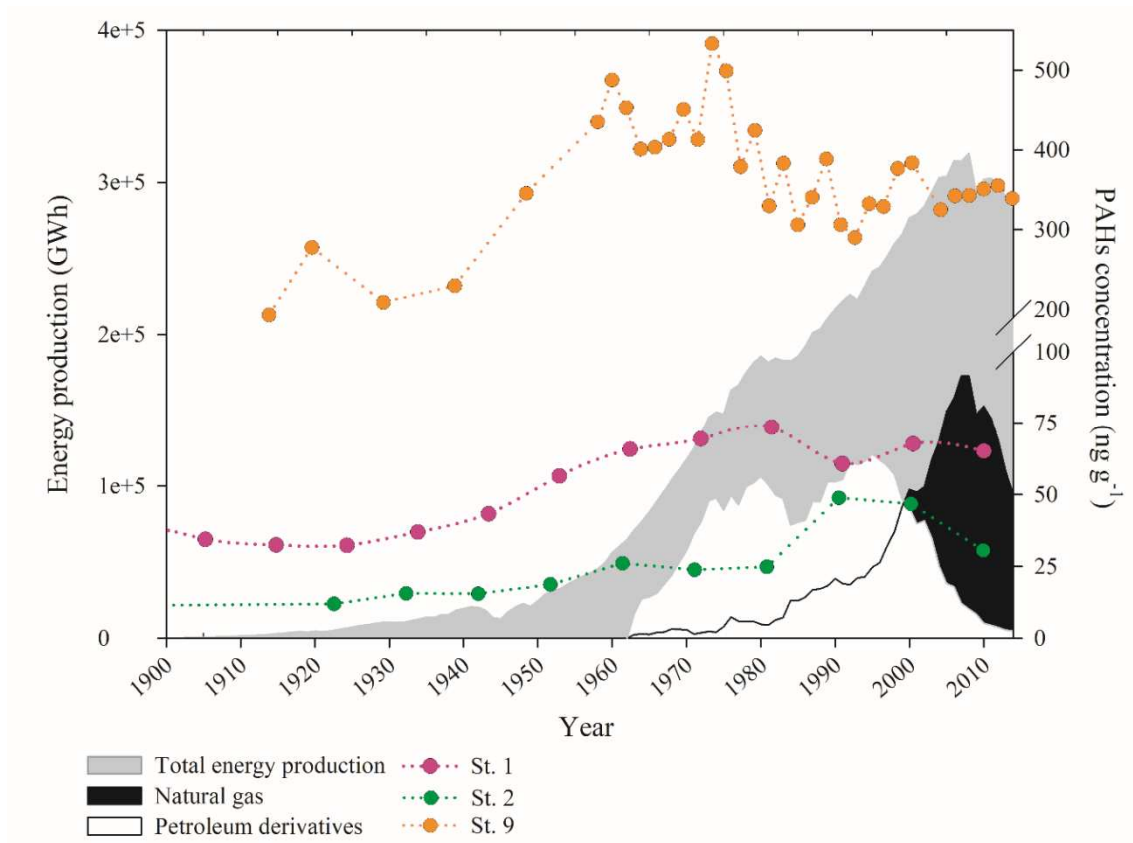


Figure 6. Historical variation of PAHs concentrations in the sediment cores from the Adriatic Sea (ng g⁻¹) and energy production (GWh) in Italy.

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: