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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<sup>-1</sup>,  $\sum_5\text{PCBs}$  ranged from 0.9 to 5.2 ng g<sup>-1</sup> and  
24  $\sum\text{DDTs}$  (*p,p'*-DDD + *p,p'*-DDE) ranged from 0.1 to 2.5 ng g<sup>-1</sup>. In the SWAM,  $\sum\text{PAHs}$   
25 ranged from 11 to 74 ng g<sup>-1</sup> 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  $152 \pm 31$  ng cm<sup>2</sup> y<sup>-1</sup> and  $0.70 \pm 0.35$  ng cm<sup>2</sup> y<sup>-1</sup> for PAHs and OCs, respectively) than  
28 in the southern Adriatic ( $2.62 \pm 0.9$  ng cm<sup>2</sup> y<sup>-1</sup> and  $0.03 \pm 0.02$  ng cm<sup>2</sup> y<sup>-1</sup> 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 19<sup>th</sup>  
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-Holocence 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  $\leq 50$  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 ( $\phi$ ) 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  $\text{cm}^{-3}$  and a water density of  $1.034$  g  $\text{cm}^{-3}$ . Grain size was determined  
150 after a pre-treatment with  $\text{H}_2\text{O}_2$  and wet sieving at  $63$   $\mu\text{m}$  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 ( $\text{C}_{\text{org}}$ ) 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<sup>-1</sup> to 180 °C, increasing at 10 °C min<sup>-1</sup> 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<sup>-1</sup>). 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 ( $\text{ng g}^{-1}$ ).

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  $0.01 \text{ ng g}^{-1}$  (PCB 138) and  $1.8 \text{ ng g}^{-1}$  (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  $C_{\text{org}}$ ) 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  $^{210}\text{Pb}$  activities. Alpha counting of daughter isotope  $^{210}\text{Po}$ , considered in  
 220 secular equilibrium with its grandparent  $\text{Ra}^{226}$ , was used for  $^{210}\text{Pb}$  analyses. Estimated  
 221 SARs ( $0.107 \text{ cm y}^{-1}$  at Station 1,  $0.100 \text{ cm y}^{-1}$  at Station 2, and  $0.52 \text{ cm y}^{-1}$  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 ( $\Sigma\text{PCBs}$ ,  $\Sigma\text{DDTs}$ , and  $\Sigma\text{PAHs}$ ) in  
 229 sediment layer  $i$  ( $\text{ng g}^{-1}$ ),  $r$  is the SAR in the sediment core ( $\text{cm y}^{-1}$ ) and  $\rho_i$  is the bulk dry  
 230 density of the sediment layer  $i$  ( $\text{g cm}^{-3}$ ).

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  $5.2 \text{ ng g}^{-1}$  ( $2.4 \pm 0.8 \text{ ng g}^{-1}$ ),  
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  $2.5 \text{ ng g}^{-1}$  ( $1.0 \pm 0.4 \text{ ng g}^{-1}$ ). 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  $0.06 \text{ ng g}^{-1}$  for  
269 PCBs and  $0.04$  to  $0.3 \text{ ng g}^{-1}$  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  $2.1 \text{ ng g}^{-1}$  ( $0.5 \pm 0.3 \text{ ng g}^{-1}$ ), and between <DL and  $1.4$   
272  $\text{ng g}^{-1}$  ( $0.3 \pm 0.3 \text{ ng g}^{-1}$ ) off the Bari canyon and at the sediment drift (stations 1 and 2),  
273 respectively. The  $\sum\text{DDTs}$  ranged from <DL to  $2.1 \text{ ng g}^{-1}$  ( $0.6 \pm 0.6 \text{ ng g}^{-1}$ ) at station 1  
274 and from <DL to  $0.7 \text{ ng g}^{-1}$  ( $0.3 \pm 0.3 \text{ ng g}^{-1}$ ) 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<sup>-1</sup> (48.3 ± 16 ng g<sup>-1</sup>) in sediment core 1 (off the Bari canyon; Figure 2); from 11  
280 to 49 ng g<sup>-1</sup> (25 ± 9 ng g<sup>-1</sup>) in sediment core 2 (sediment drift; Figure 3); and from 193  
281 to 533 ng g<sup>-1</sup> (mean ± SD of 363 ± 59 ng g<sup>-1</sup>) 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 cm<sup>2</sup> y<sup>-1</sup> and from 0 to 0.1 ng cm<sup>2</sup> y<sup>-1</sup> in stations 1 and 2,  
306 respectively) in comparison to the northern Adriatic (0.02 to 2.2 ng cm<sup>2</sup> y<sup>-1</sup>; 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<sup>-1</sup>,  
312 0.7 ng g<sup>-1</sup>, and 5.2 ng g<sup>-1</sup> in stations 1, 2, and 9) and  $\sum$ DDTs (2.1 ng g<sup>-1</sup>, 0.7 ng g<sup>-1</sup>,  
313 and 2.5 ng g<sup>-1</sup> 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<sup>-1</sup>, <LQ, and 2.7 ng g<sup>-1</sup> and DDT presented concentrations of  
316 0.7 ng g<sup>-1</sup>, 0.6 ng g<sup>-1</sup>, and 0.9 ng g<sup>-1</sup> 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 cm<sup>2</sup> y<sup>-1</sup>) in the Po River prodelta  
319 (station 9), followed by off the Bari canyon (station 1; 3.2 ± 0.9 ng cm<sup>2</sup> y<sup>-1</sup>) and the  
320 sediment drift (station 2; 1.8 ± 0.5 ng cm<sup>2</sup> y<sup>-1</sup>). 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<sup>-1</sup>,  
323 16 ± 4 ng g<sup>-1</sup>, and 227 ± 26 ng g<sup>-1</sup> 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<sup>-1</sup>, 48 ± 1 ng g<sup>-1</sup>, and 392 ± 32 ng g<sup>-1</sup> 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  $\Sigma$ PCBs,  
338  $\Sigma$ DDTs, and  $\Sigma$ 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  $346 \text{ ng g}^{-1}$ ;  
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  $\Sigma_5$ 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 19<sup>th</sup> 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).  $\Sigma$ PAH,  $\Sigma$ PCB and  $\Sigma$ 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  $\Sigma$ DDT and  $\Sigma$ 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 20<sup>th</sup> 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 19<sup>th</sup> 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 m<sup>3</sup>s<sup>-1</sup> 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 m<sup>3</sup> s<sup>-1</sup>; 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 m<sup>3</sup>s<sup>-1</sup> 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  $\Sigma$ 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  $\Sigma$ DDT and  $\Sigma$ 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  $\Sigma$ DDT and  
490  $\Sigma$ 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  $\Sigma$ DDT and  $\Sigma$ 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 21<sup>st</sup> 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

### 542 **References**

- 543 Alebic-Juretic, A., 2011. Polycyclic aromatic hydrocarbons in marine sediments from  
544 the Rijeka Bay area, Northern Adriatic, Croatia, 1998-2006. *Mar. Pollut. Bull.* 62,  
545 863–869.
- 546 Artegiani, A., Bregant, D., Paschini, E., Pinardi, N., Raicich, F., Russo, A., 1997. The  
547 Adriatic Sea general circulation. Part II: Baroclinic circulation structure. *J. Phys.*  
548 *Oceanogr.* 27, 1515–1532.
- 549 ARPA (Agenzia Regionale Prevenzione e Ambiente dell’Emilia Romagna), 2014.  
550 *Annali Idrologici of Arpa Emilia-Romagna*. Available at: <http://www.arpa.emr.it>.
- 551 Baek, S.Y., Choi, S.D., Park, H., Kang, J.H., Chang, Y.S., 2010. Spatial and Seasonal  
552 Distribution of Polychlorinated Biphenyls (PCBs) in the Vicinity of an Iron and Steel  
553 Making Plants. *Environ. Sci. Technol.* 44, 3035–3040.

- 554 Bartlett, P.W., Isaksson, E., Hermanson, M.H., 2019. 'New' unintentionally produced  
555 PCBs in the Arctic. *Emerging Contaminants* 5, 9-14.
- 556 Boldrin, A., Langone, L., Miserocchi, S., Turchetto, M., Acri, F., 2005. Po River plume  
557 on the Adriatic continental shelf: Dispersion and sedimentation of dissolved and  
558 suspended matter during different river discharge rates. *Marine Geology* 222–223,  
559 135–158.
- 560 Boonyatumanond, R., Wattayakorn, G., Amano, A., Inouchi, Y., Takada, H., 2007.  
561 Reconstruction of pollution history of organic contaminants in the upper Gulf of  
562 Thailand by using sediment cores: first report from Tropical Asia Core (TACO)  
563 project. *Mar. Pollut. Bull.* 54, 554–65.
- 564 Bossi, R., Larsen, B., Premazzi, G., 1992. Polychlorinated biphenyl congeners and other  
565 chlorinated hydrocarbons in bottom sediment cores of Lake Garda (Italy). *Sci. Total*  
566 *Environ.* 121, 77–93.
- 567 Breivik, K., Alcock, R., Li, Y.F., Bailey, R.E., Fiedler, H., Pacyna, J.M., 2004. Primary  
568 sources of selected POPs: regional and global scale emission inventories. *Environ.*  
569 *Pollut.* 128, 3–16.
- 570 Breivik, K., Sweetman, A., Pacyna, J.M., Jones, K.C., 2007. Towards a global historical  
571 emission inventory for selected PCB congeners — A mass balance approach 3. An  
572 update. *Sci. Total Environ.* 377, 199–224.
- 573 Breivik, K., Sweetman, A., Pacyna, J.M., Jones, K.C., 2002. Towards a global historical  
574 emission inventory for selected PCB congeners — a mass balance approach 2.  
575 Emissions. *Sci. Total Environ.* 290, 296–307.
- 576 Breivik, K., Armitage, J.M., Wania, F., Sweetman, A.J., Jones, K.C., 2016. Tracking the  
577 Global Distribution of Persistent Organic Pollutants Accounting for E□Waste  
578 Exports to Developing Regions. *Environ. Sci. Technol.* 50, 798–805.
- 579 Cai, Y., Wang, X., Wu, Y., Li, Y., Ya, M., 2016. Over 100-year sedimentary record of  
580 polycyclic aromatic hydrocarbons (PAHs) and organochlorine compounds (OCs) in  
581 the continental shelf of the East China Sea. *Environ. Pollut.* 219, 774–784.
- 582 Caricchia, A.M., IcciaChiavarini, S., Cremisini, C., Martini, F., Morabito, R., 1993.  
583 PAHs, PCBs, and DDE in the northern Adriatic Sea. *Mar. Pollut. Bull.* 26, 581–583.
- 584 Cattaneo, A., Trincardi, F., Asioli, A., Correggiari, A., 2007. The Western Adriatic shelf  
585 clinoform: energy-limited bottomset. *Cont. Shelf Res.* 27, 506–525.
- 586 Combi, T., Martins, C.C., Taniguchi, S., Leonel, J., Lourenço, R.A., Montone, R.C.,  
587 2017. Depositional history and inventories of polychlorinated biphenyls (PCBs) in  
588 sediment cores from an Antarctic Specially Managed Area (Admiralty Bay, King  
589 George Island). *Mar. Pollut. Bull.* 118, 447–451.

- 590 Combi, T., Miserocchi, S., Langone, L., Guerra, R., 2016. Polychlorinated biphenyls  
591 (PCBs) in sediments from the western Adriatic Sea: Sources, historical trends and  
592 inventories. *Sci. Total Environ.* 562, 580–587.
- 593 de Boer, J., Leslie, H., van Leeuwen, S.P.J., Wegener, J.-W., van Bavel, B., Lindström,  
594 G., Lahoutifard, N., Fiedler, H., 2008. United Nations Environment Programme  
595 Capacity Building Pilot Project--training and interlaboratory study on persistent  
596 organic pollutant analysis under the Stockholm Convention. *Anal. Chim. Acta* 617,  
597 208–15.
- 598 European Commission, 2013. Directive 2013/39/EU of the European Parliament and of  
599 the Council of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC  
600 as regards priority substances in the field of water policy.
- 601 Franců, E., Schwarzbauer, J., Lána, R., Nývlt, D., Nehyba, S., 2009. Historical Changes  
602 in Levels of Organic Pollutants in Sediment Cores from Brno Reservoir, Czech  
603 Republic. *Water, Air, Soil Pollut.* 209, 81–91.
- 604 Frignani, M., Langone, L., Ravaioli, M., Sorgente, D., Alvisi, F., Albertazzi, S., 2005.  
605 Fine-sediment mass balance in the western Adriatic continental shelf over a century  
606 time scale. *Mar. Geol.* 222–223, 113–133.
- 607 Garmash, O., Hermanson, M. H., Isaksson, E., Schwikowski, M., Divine, D., Teixeira,  
608 C., Muir, D. C. G., 2013. Deposition history of polychlorinated biphenyls to the  
609 Lomonosovfonna glacier, Svalbard: A 209 congener analysis. *Environ. Sci. Technol.*,  
610 47, 12064–12072.
- 611 Geisz, H.N., Dickhut, R.M., Cochran, M. a., Fraser, W.R., Ducklow, H.W., 2008.  
612 Melting Glaciers: A Probable Source of DDT to the Antarctic Marine Ecosystem.  
613 *Environ. Sci. Technol.* 42, 3958–3962.
- 614 Giuliani, S., Bellucci, L.G., Çağatay, M.N., Polonia, A., Piazza, R., Vecchiato, M.,  
615 Pizzini, S., Gasperini, L., 2017. The impact of the 1999 Mw 7.4 event in the İzmit  
616 Bay (Turkey) on anthropogenic contaminant (PCBs, PAHs and PBDEs)  
617 concentrations recorded in a deep sediment core. *Sci. Total Environ.* 590–591, 799–  
618 808.
- 619 Guerra, R., Pasteris, A., Righi, S., Ok, G., 2019. Historical record of polychlorinated  
620 biphenyls (PCBs) in the continental shelf of the Korea Strait. *Chemosphere* 237,
- 621 Guzzella, L., Paolis, A. de, 1994. Polycyclic Aromatic Hydrocarbons in Sediments of  
622 the Adriatic Sea. *Mar. Pollut. Bull.* 28, 159–165.
- 623 Holoubek, I., Klánová, J., 2008. Spatial and Temporal Trends of Global, Regional, and  
624 Local POPs Distribution, in: Mehmetli, E., Koumanova, B. (Eds.), *The Fate of*  
625 *Persistent Organic Pollutants in the Environment.* Springer Netherlands, pp. 219–  
626 228.
- 627 Hornbuckle, K., Robertson, L., 2010. Polychlorinated Biphenyls (PCBs): Sources,  
628 Exposures, Toxicities. *Environ. Sci. Technol.* 44, 2749–2751.

- 629 Hosoda, J., Ofosu-Anim, J., Sabi, E.B., Akita, L.G., Onwona-Agyeman, S., Yamashita,  
630 R., Takada, H., 2014. Monitoring of organic micropollutants in Ghana by  
631 combination of pellet watch with sediment analysis: E-waste as a source of PCBs.  
632 *Mar. Pollut. Bull.* 2009, 0–6.
- 633 Hu, D.F. and Hornbuckle, K.C., 2010. Inadvertent Polychlorinated Biphenyls in  
634 Commercial Paint Pigments. *Environ. Sci. Technol.* 44, 2822–2827
- 635 Jafarabadi, A.R., Bakhtiari, A.R., Aliabadian, M., Toosi, A.S., 2017a. Spatial  
636 distribution and composition of aliphatic hydrocarbons, polycyclic aromatic  
637 hydrocarbons and hopanes in superficial sediments of the coral reefs of the Persian  
638 Gulf, Iran. *Environ. Pollut.* 224, 195–223.
- 639 Jafarabadi, A.R., Bakhtiari, A.R., Toosi, A.S., 2017b. Comprehensive and comparative  
640 ecotoxicological and human risk assessment of polycyclic aromatic hydrocarbons  
641 (PAHs) in reef surface sediments and coastal seawaters of Iranian Coral Islands,  
642 Persian Gulf. *Ecotoxicol. Environ. Saf.* 145, 640–652.
- 643 Kannan, K., Johnson-Restrepo, B., Yohn, S.S., Giesy, J.P., Long, D.T., 2005. Spatial  
644 and temporal distribution of polycyclic aromatic hydrocarbons in sediments from  
645 Michigan inland lakes. *Environ. Sci. Technol.* 39, 4700–6.
- 646 Kwan, C.S., Takada, H., Boonyatumanond, R., Kato, Y., Mizukawa, K., Ito, M., Dung,  
647 L.Q., Zakaria, M.P., Santiago, E.C., 2014. Historical occurrences of polybrominated  
648 diphenyl ethers and polychlorinated biphenyls in Manila Bay, Philippines, and in the  
649 upper Gulf of Thailand. *Sci. Total Environ.* 470-471, 427-437..
- 650 Liu, L.Y., Wang, J.Z., Wei, G.L., Guan, Y.F., Wong, C.S., Zeng, E.Y., 2012. Sediment  
651 records of Polycyclic Aromatic Hydrocarbons (PAHs) in the continental shelf of  
652 China: Implications for evolving anthropogenic impacts. *Environ. Sci. Technol.* 46,  
653 6497–6504.
- 654 Lohmann, R., Breivik, K., Dachs, J., Muir, D., 2007. Global fate of POPs: Current and  
655 future research directions. *Environ. Pollut.* 150, 150–165.
- 656 Long, ER, Field, L. and D.M., 1998. Predicting Toxicity in Marine Sediments with  
657 Numerical Sediment Quality Guidelines. *Environ. Toxicol. Chem.* 17, 714–727.
- 658 Long, E.R., MacDonald, D.D., Smith, S.L., Calder, F.D., 1995. Incidence of Adverse  
659 Biological Effects within Ranges of Chemical Concentrations in Marine and  
660 Estuarine Sediments. *Environ. Manage.* 81–97.
- 661 Macdonald, D.D., Ingersoll, C.G., Berger, T.A., 2000. Development and evaluation of  
662 consensus-based sediment quality guidelines for freshwater ecosystems. *Arch.*  
663 *Environ. Contam. Toxicol.* 31, 20–31.
- 664 Magi, E., Bianco, R., Ianni, C., Di Carro, M., 2002. Distribution of polycyclic aromatic  
665 hydrocarbons in the sediments of the Adriatic Sea. *Environ. Pollut.* 119, 91–98.

- 666 Manca, B.B., Kovaevi, V., Gai, M., Viezzoli, D., 2002. Dense water formation in the  
667 Southern Adriatic Sea and spreading into the Ionian Sea in the period 1997-1999. *J.*  
668 *Mar. Syst.* 33–34, 133–154.
- 669 Mandalakis, M., Polymenakou, P.N., Tselepidis, A., Lampadariou, N., 2014.  
670 Distribution of aliphatic hydrocarbons, polycyclic aromatic hydrocarbons and  
671 organochlorinated pollutants in deep-sea sediments of the Southern Cretan margin,  
672 Eastern Mediterranean Sea: a baseline assessment. *Chemosphere* 106, 28–35.
- 673 Martins, C.C., Bicego, M.C., Rose, N.L., Taniguchi, S., Lourenço, R.A., Figueira,  
674 R.C.L., Mahiques, M.M., Montone, R.C., 2010. Historical record of polycyclic  
675 aromatic hydrocarbons (PAHs) and spheroidal carbonaceous particles (SCPs) in  
676 marine sediment cores from Admiralty Bay, King George Island, Antarctica.  
677 *Environ. Pollut.* 158, 192–200.
- 678 Matsumura, F., 2009. DTT, in: Resh, V.H., Cardé, R.T. (Eds.), *Encyclopedia of Insects.*  
679 Academic Press, pp. 251–252.
- 680 Merhaby, D., Net, S., Halwani, J., Ouddane, B., 2015. Organic pollution in surficial  
681 sediments of Tripoli harbour, Lebanon. *Mar. Pollut. Bull.* 93, 284–293.
- 682 Mourier, B., Desmet, M., Van Metre, P.C., Mahler, B.J., Perrodin, Y., Roux, G., Bedell,  
683 J.-P., Lefèvre, I., Babut, M., 2014. Historical records, sources, and spatial trends of  
684 PCBs along the Rhône River (France). *Sci. Total Environ.* 476–477, 568–76.
- 685 Neves, P.A., Colabuono, F.I., Ferreira, P.A.L., Kawakami, S.K., Taniguchi, S., Figueira,  
686 R.C.L., Mahiques, M.M., Montone, R.C., Bicego, M.C., 2018. Depositional history  
687 of polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs) and  
688 polycyclic aromatic hydrocarbons (PAHs) in an Amazon estuary during the last  
689 century. *Sci. Total Environ.* 615, 1262–1270.
- 690 Nizzetto, L., Macleod, M., Borgå, K., Cabrerizo, A., Dachs, J., Di Guardo, A.,  
691 Ghirardello, D., Hansen, K.M., Jarvis, A., Lindroth, A., Ludwig, B., Monteith, D.,  
692 Perlinger, J. a, Scheringer, M., Schwendenmann, L., Semple, K.T., Wick, L.Y.,  
693 Zhang, G., Jones, K.C., 2010. Past, present, and future controls on levels of persistent  
694 organic pollutants in the global environment. *Environ. Sci. Technol.* 44, 6526–6531.
- 695 Palinkas, C.M., Nittrouer, C. a., 2007. Modern sediment accumulation on the Po shelf,  
696 Adriatic Sea. *Cont. Shelf Res.* 27, 489–505.
- 697 Parolini, M., Binelli, A., Matozzo, V., Marin, M.G., 2010. Persistent organic pollutants  
698 in sediments from the Lagoon of Venice—a possible hazard for sediment-dwelling  
699 organisms. *J. Soils Sediments* 10, 1362–1379.
- 700 Pavlova, P.A., Jenk, T.M., Schmid, P., Bogdal, C., Steinlin, C., Schwikowski, M., 2015.  
701 Polychlorinated Biphenyls in a Temperate Alpine Glacier: 1. Effect of Percolating  
702 Meltwater on their Distribution in Glacier Ice. *Environ. Sci. Technol.* 49,  
703 14085–14091.

- 704 Pérez-Fernández, B., Viñas, L., Bargiela, J., 2016. Historical Profiles of Polycyclic  
705 Aromatic Hydrocarbons (PAHs) in Marine Sediment Cores from Northwest Spain.  
706 Arch. Environ. Contam. Toxicol. 71, 439–453.
- 707 Pintado-Herrera, M.G., González-Mazo, E., Lara-Martín, P.A., 2016. In-cell clean-up  
708 pressurized liquid extraction and gas chromatography–tandem mass spectrometry  
709 determination of hydrophobic persistent and emerging organic pollutants in coastal  
710 sediments. J. Chromatogr. A 1429, 107–118.
- 711 Pouch, A., Zaborska, A., Pazdro, K., 2017. Concentrations and origin of polychlorinated  
712 biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) in sediments of  
713 western Spitsbergen fjords (Kongsfjorden, Hornsund, and Adventfjorden). Environ.  
714 Monit. Assess. 189.
- 715 Pozo, K., Lazzarini, D., Perra, G., Volpi, V., Corsolini, S., Focardi, S., 2009. Levels and  
716 spatial distribution of polychlorinated biphenyls (PCBs) in superficial sediment from  
717 15 Italian Marine Protected Areas (MPA). Mar. Pollut. Bull. 58, 773–776.
- 718 Readman, J.W., Fillmann, G., Tolosa, I., Bartocci, J., Villeneuve, J.P., Catinni, C., Mee,  
719 L.D., 2002. Petroleum and PAH contamination of the Black Sea. Mar. Pollut. Bull.  
720 44, 48–62.
- 721 Romano, S., Langone, L., Frignani, M., Albertazzi, S., Focaccia, P., Bellucci, L.G.,  
722 Ravaioli, M., 2013. Historical pattern and mass balance of trace metals in sediments  
723 of the northwestern Adriatic Sea Shelf. Mar. Pollut. Bull. 76, 32–41.
- 724 Schulz, D.E., Petrich, G., Duinker, J.C., 1989. Complete Characterization of  
725 Polychlorinated Biphenyl Congeners in Commercial Aroclor and Clophen Mixtures  
726 by Multidimensional Gas Chromatography-Electron Capture Detection. Environ. Sci.  
727 Technol. 23, 852–859.
- 728 Smith, N., Lee, K., Gobeil, C., Macdonald, R.W., 2009. Natural rates of sediment  
729 containment of PAH, PCB and metal inventories in Sydney Harbour, Nova Scotia.  
730 Sci. Total Environ. 407, 4858–4869.
- 731 Sobek, A., Sundqvist, K.L., Assefa, A.T., Wiberg, K., 2015. Baltic Sea sediment  
732 records: Unlikely near-future declines in PCBs and HCB. Sci. Total Environ. 518–  
733 519, 8–15.
- 734 Soper, F. L., Davis, W. A., Markham, F., Riehl, L. A., 1947. Typhus Fever in Italy,  
735 1943-1945, and its Control with Louse Powder. The American Journal Of Hygiene  
736 45(3), 305-334.
- 737 Sun, Y. Yuan, G.L., Li, J., Tang, J., Wang, G.H., 2018. High-resolution sedimentary  
738 records of some organochlorine pesticides in Yamzho Yumco Lake of the Tibetan  
739 Plateau: Concentration and composition. Sci Total Environ 615, 469–475.
- 740 Tesi, T., Langone, L., Giani, M., Ravaioli, M., Miserocchi, S., 2013. Source, diagenesis,  
741 and fluxes of particulate organic carbon along the western adriatic Sea  
742 (mediterranean Sea). Mar. Geol. 337, 156–170.

- 743 Tesi, T., Miserocchi, S., Goñi, M. a., Langone, L., Boldrin, a., Turchetto, M., 2007.  
744 Organic matter origin and distribution in suspended particulate materials and  
745 surficial sediments from the western Adriatic Sea (Italy). *Estuar. Coast. Shelf Sci.* 73,  
746 431–446.
- 747 Turchetto, M., Boldrin, a., Langone, L., Miserocchi, S., Tesi, T., Foglini, F., 2007.  
748 Particle transport in the Bari Canyon (southern Adriatic Sea). *Mar. Geol.* 246, 231–  
749 247.
- 750 Vallack, H.W., Bakker, D.J., Brandt, I., Brostro, E., Brouwer, A., Bull, K.R., Gough, C.,  
751 Guardans, R., Holoubek, I., Mccutcheon, P., Mocarelli, P., Taalman, R.D.F., 1998.  
752 Controlling persistent organic pollutants – what next ? *Environ. Toxicol. Pharmacol.*  
753 6, 143–175.
- 754 Viganò, L., Mascolo, G., Roscioli, C., 2015. Emerging and priority contaminants with  
755 endocrine active potentials in sediments and fish from the River Po (Italy). *Environ.*  
756 *Sci. Pollut. Res.* 22, 14050–66.
- 757 Wheeler, C. M., 1946. Control of typhus in Italy, 1943-1944, by use of DDT. *Amer.*  
758 *Jour. Pub. Health* 36, 119-129.
- 759 Yunker, M.B., Macdonald, R.W., Vingarzan, R., Mitchell, R.H., Goyette, D., Sylvestre,  
760 S., 2002. PAHs in the Fraser River basin: A critical appraisal of PAH ratios as  
761 indicators of PAH source and composition. *Org. Geochem.* 33, 489–515.
- 762 Zaborska, A., Carroll, J., Pazdro, K., Pempkowiak, J., 2011. Spatio-temporal patterns of  
763 PAHs, PCBs and HCB in sediments of the western Barents sea. *Oceanologia* 53,  
764 1005–
- 765 Zhang, G., Parker, A., House, A., Mai, B., Li, X., Kang, Y., Wang, Z., 2002.  
766 Sedimentary records of DDT and HCH in the Pearl River Delta, South China.  
767 *Environ. Sci. Technol.* 36, 3671–7.

**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<sup>-1</sup> dry weight)

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

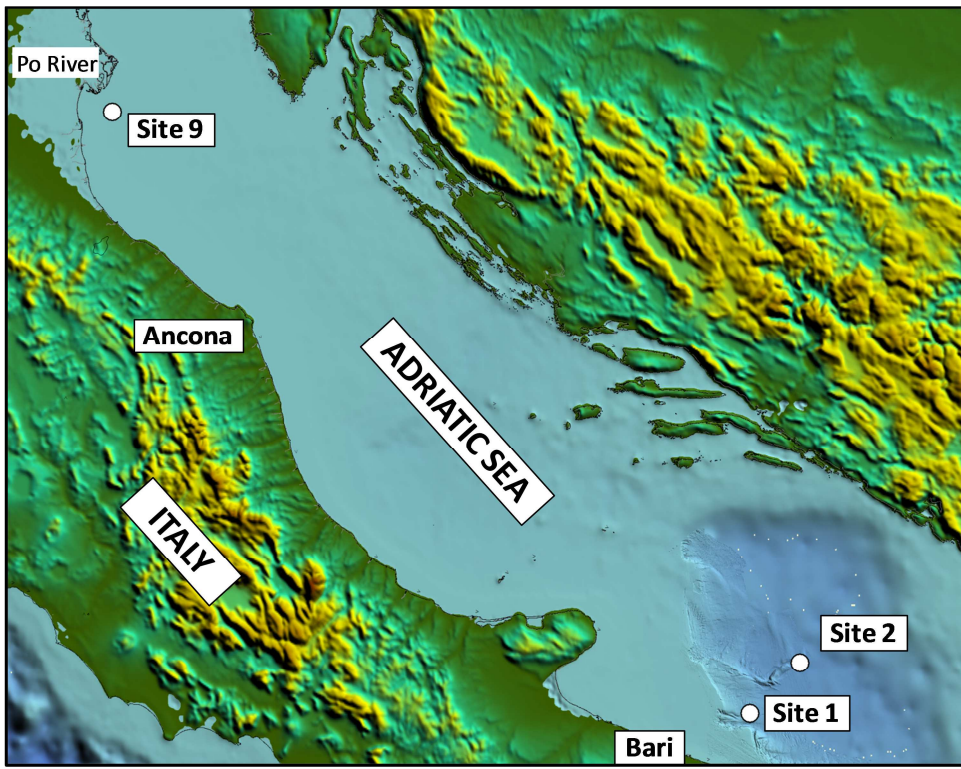
<sup>a</sup>: ∑<sub>16</sub>PAHs; <sup>b</sup>: ∑<sub>12</sub>PAHs; <sup>c</sup>: ∑<sub>10</sub>PAHs; <sup>d</sup>: ∑<sub>35</sub>PAHs; <sup>e</sup>: ∑<sub>15</sub>PAHs; <sup>f</sup>: ∑<sub>18</sub>PAHs

<sup>g</sup>: ∑<sub>5</sub>PCBs; <sup>h</sup>: not informed; <sup>i</sup>: ∑<sub>127</sub>PCBs; <sup>j</sup>: ∑<sub>20</sub>PCBs; <sup>k</sup>: ∑<sub>24</sub>PCBs; <sup>l</sup>: ∑<sub>7</sub>PCBs

<sup>m</sup>: ∑p,p'-DDT, p,p'-DDD, p,p'-DDE; <sup>n</sup>: DDE; <sup>o</sup>: ∑p,p'-DDT, p,p'-DDD, p,p'-DDE, o,p'-DDT, o,p'-DDD, o,p'-DDE

DL: detection limit

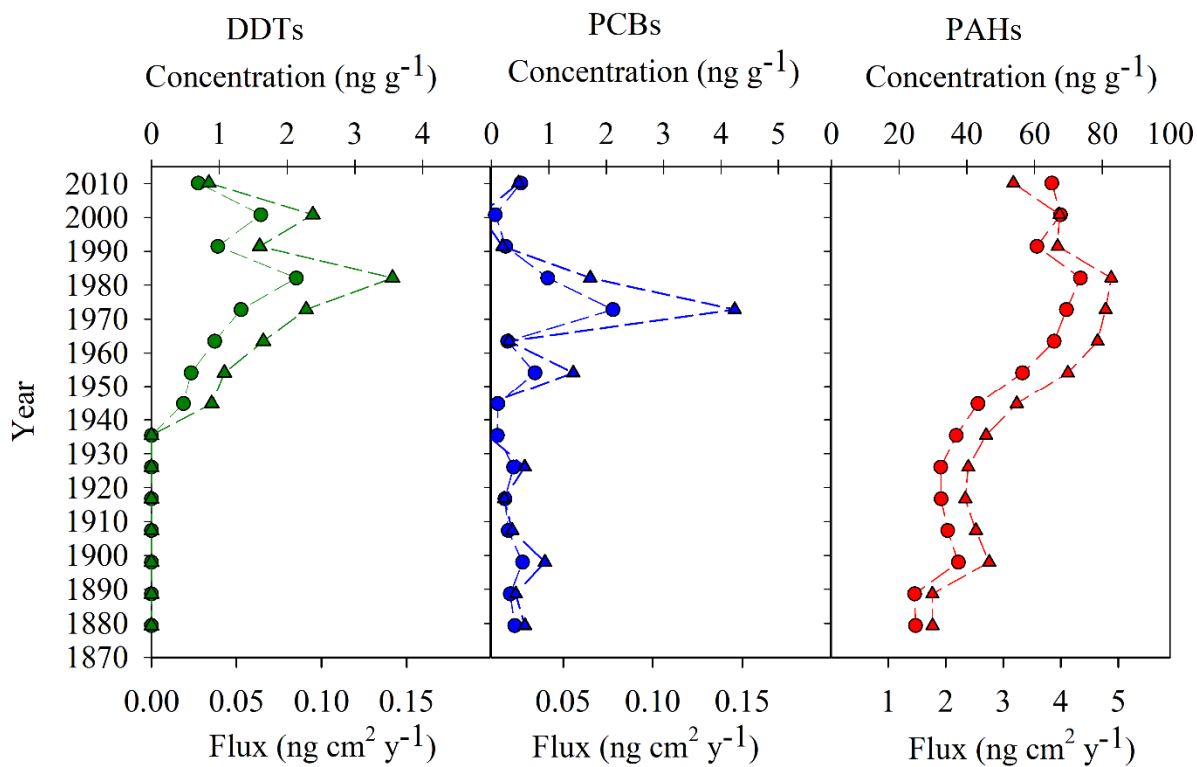
in sediment cores from other locations.



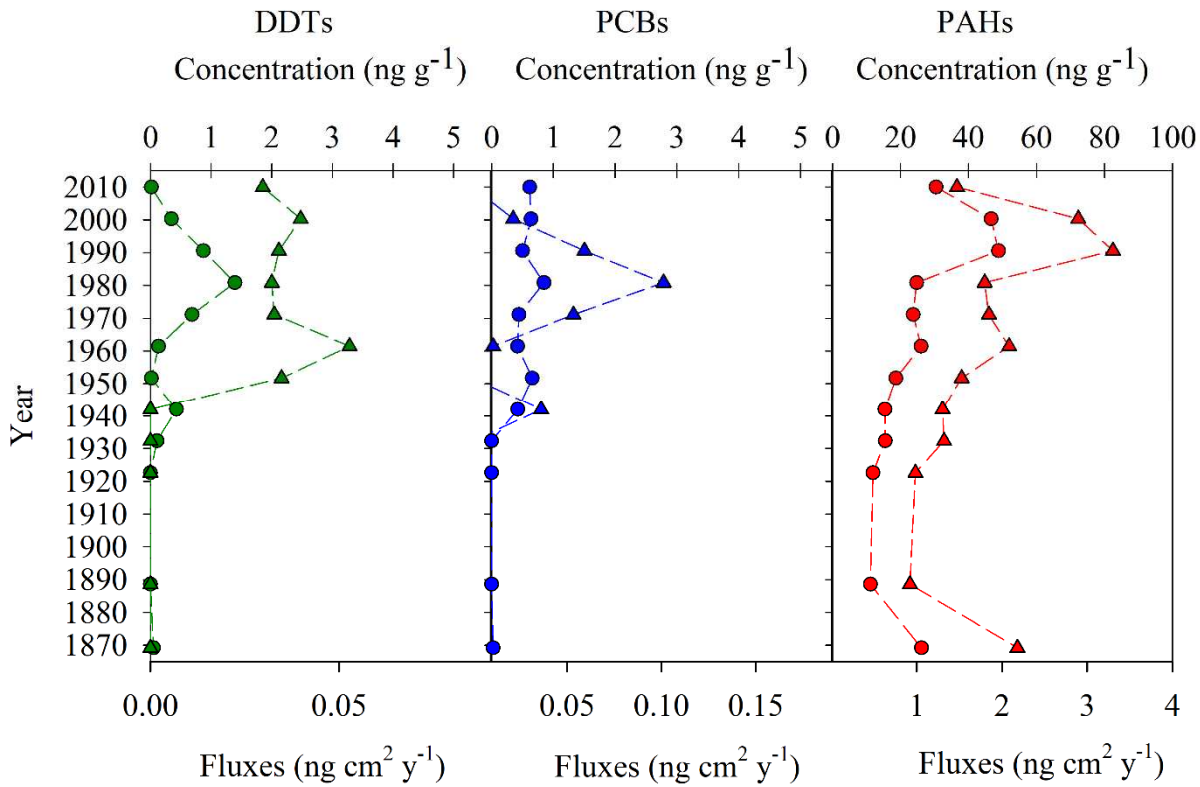
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**Figure 1.** Map of the study area showing the sampling stations in the Adriatic Sea.

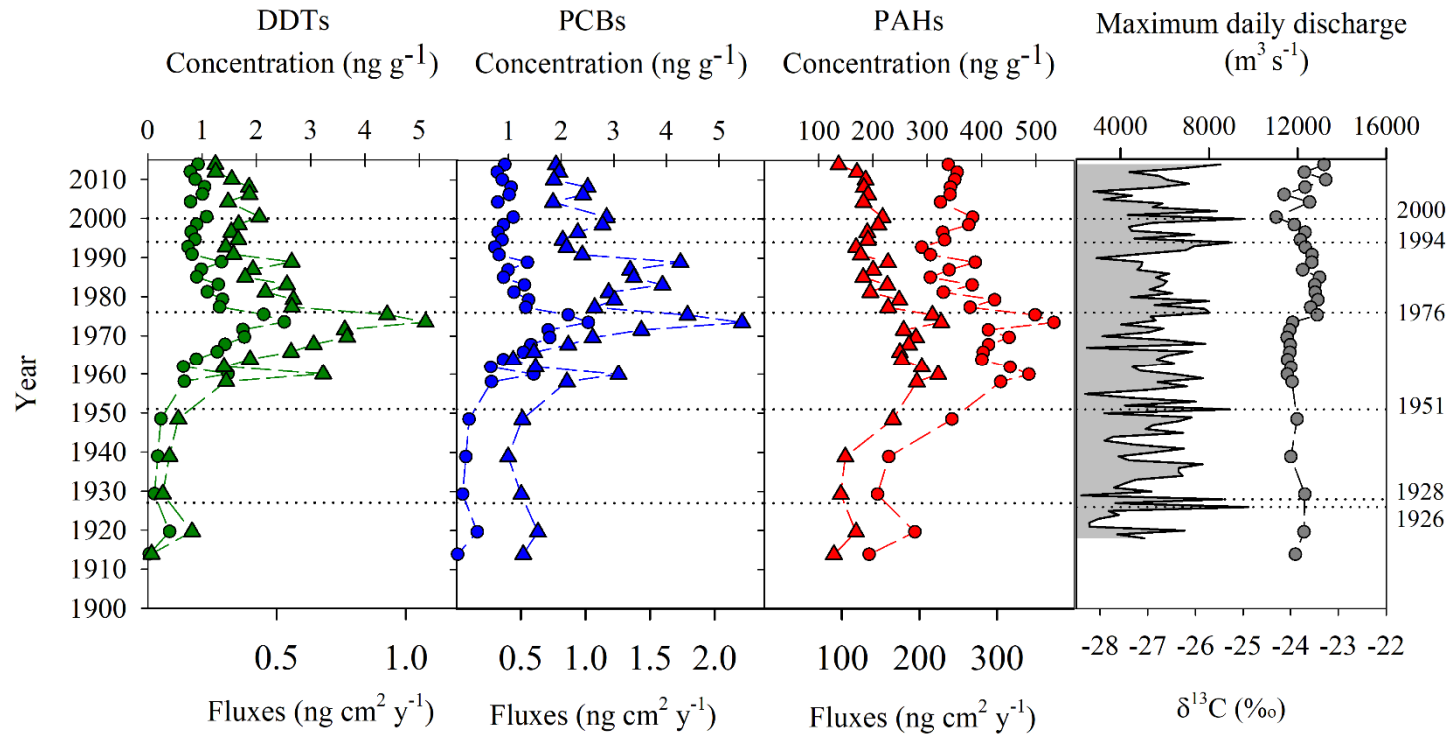
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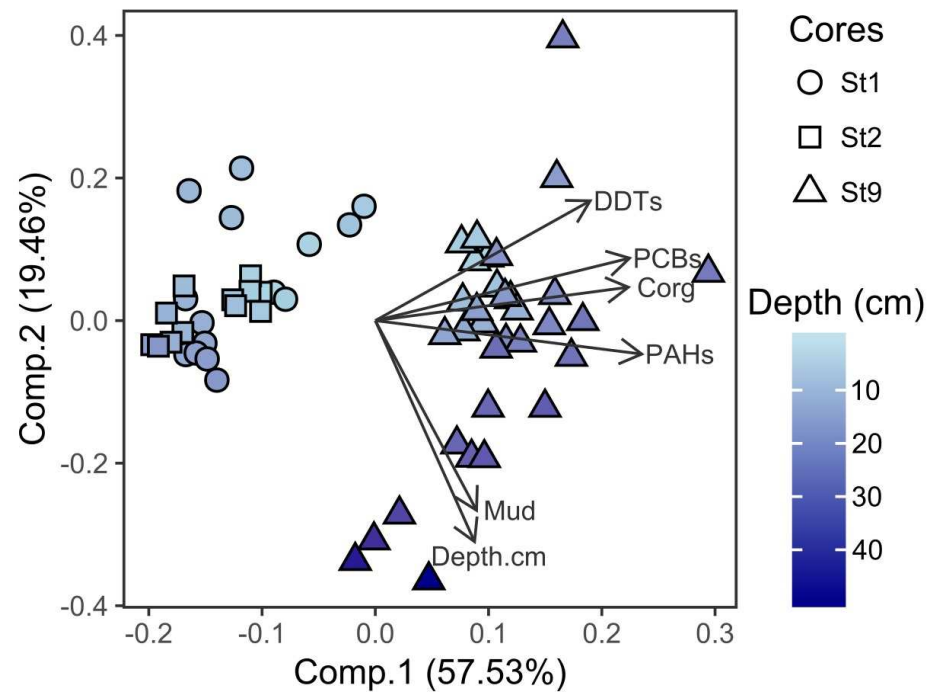
**Figure 2.** Historical records of PAHs, DDTs and PCBs in sediment cores taken off the Bari canyon (station 1) on deep South-Western Adriatic Margin (SWAM). Circles represent contaminant concentrations (ng g<sup>-1</sup>) and triangles represent contaminant fluxes (ng cm<sup>2</sup> y<sup>-1</sup>).



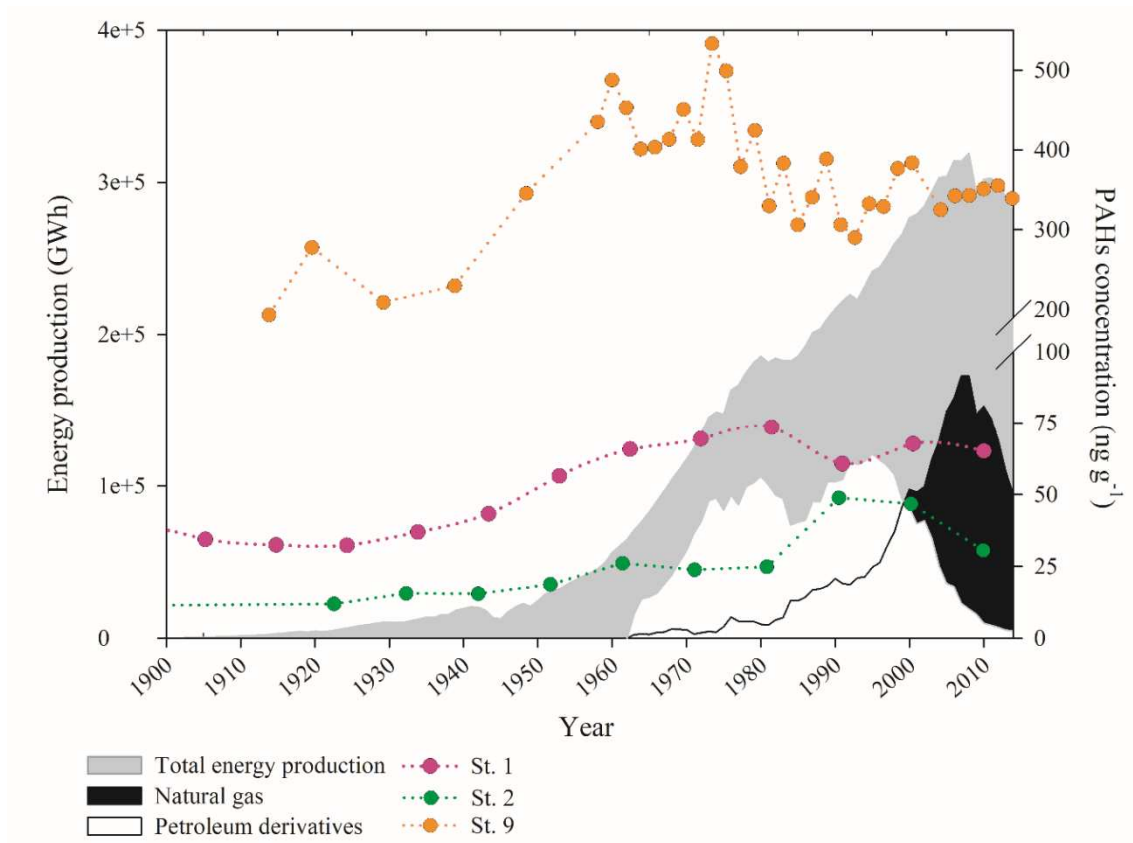
**Figure 3.** Historical records of PAHs, DDTs and PCBs in sediment cores taken in the Sediment Drift (station 2) on deep South-Western Adriatic Margin (SWAM). Circles represent contaminant concentrations (ng g<sup>-1</sup>) and triangles represent contaminant fluxes (ng cm<sup>2</sup> y<sup>-1</sup>).



**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 ( $\text{ng g}^{-1}$ ) and triangles represent contaminant fluxes ( $\text{ng cm}^2 \text{ y}^{-1}$ ).



**Figure 5.** Principal component analysis (PCA) plot of contaminant ( $\Sigma$ PAHs,  $\Sigma$ PCBs, and  $\Sigma$ 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 ( $\text{ng g}^{-1}$ ) 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: