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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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	Journal Pre-proof					
1	Historical sedimentary deposition and flux of PAHs, PCBs and DDTs in sediment					
2	cores from the western Adriatic Sea					
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### 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.  $\Sigma_{16}$ PAHs ranged from 193 to 533 ng g<sup>-1</sup>,  $\Sigma_5$ PCBs ranged from 0.9 to 5.2 ng g<sup>-1</sup> and 23  $\Sigma$ DDTs (*p*,*p'*-DDD + *p*,*p'*-DDE) ranged from 0.1 to 2.5 ng g<sup>-1</sup>. In the SWAM,  $\Sigma$ PAHs 24 ranged from 11 to 74 ng g<sup>-1</sup> while  $\Sigma$ PCB and  $\Sigma$ DDT concentrations were close to the 25 26 MQL. Accordingly, contaminant fluxes were much higher in the northern (mean values 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 27 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 28 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 consumption (from petroleum derivatives to natural gas) in Italy from the end of the 19<sup>th</sup> 31 century to the present. Similarly, vertical variations in DDT concentrations matched its 32 33 historical use and consumption in Italy, which started around in the mid- late 1940s to fight typhus during the II World War. Contaminant concentrations detected in 34 sediments does not seem to pose ecotoxicological risk for marine organisms in the 35 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 countries in the Southern Hemisphere, though current world usage is small (~1kt  $y^{-1}$ ) 55 compared with historical use (>40kt v<sup>-1</sup>) from 1950 to 1980 (de Boer et al., 2008; Geisz 56 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

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

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 to target for reduction or elimination, such as volatilization from old stockpiles or from 75 old equipment that is still in use (Breivik et al., 2002; Nizzetto et al., 2010). 76 Additionally, these compounds are highly persistent in the environment and continue to 77 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 Hornbuckle, 2010), from thermal sources (e.g. steel making processes; Baek et al, 2010) 85 86 and e-waste (Breivik et al., 2016), or from melting glaciers and the cryosphere affected by climate change-related processes (Sun et al., 2018; Pavlova et al., 2015). Therefore, 87 88 it is essential to understand the temporal trends of contaminant loads into the

environment, in order to both assess the effects of environmental legislation and toidentify 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 identification is of significant environmental concern. 98

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 Adriatic can reach up to 1200 m depth in the South Adriatic Pit (Artegiani et al., 1997; 115 116 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 Por 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).

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

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 density of 2.6 g cm<sup>-3</sup> and a water density of 1.034 g cm<sup>-3</sup>. Grain size was determined 149 after a pre-treatment with  $H_2O_2$  and wet sieving at 63 µm to separate sands from fine 150 151 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 (Corg) was measured on decarbonated samples (1 M HCl). Stable isotopic analyses of organic C ( $\delta^{13}$ C) were carried out on the same samples using 154 a FINNIGAN Delta Plus mass spectrometer directly coupled to the FISONS NA2000 155 EA by means of a CONFLO interface for continuous flow measurements. 156

157

158 2.4. Extraction and clean-up

159 Sediments were extracted using an accelerated solvent extraction ASE 200 system160 (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 were centrifuged (10000 170 for 10 minutes) and filtered in extracts rpm 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, increasing at 25 °C min<sup>-1</sup> to 180 °C, increasing at 10 °C min<sup>-1</sup> to 300 °C, holding this 179 180 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 target compound at different concentrations (from 5 to 500 ng g<sup>-1</sup>). Target compounds 182 183 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 (p,p'-DDE + p,p'-DDD) and DDT for DDTs, and sum of 16 unsubstituted compounds 194 for PAHs (ng  $g^{-1}$ ). 195

196

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

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

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 assessed in the northern Adriatic Sea, different datasets were combined based on 214 215 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 measured for <sup>210</sup>Pb activities. Alpha counting of daughter isotope <sup>210</sup>Po, considered in 219 secular equilibrium with its grandparent Ra<sup>226</sup>, was used for <sup>210</sup>Pb analyses. Estimated 220 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) 221 were used to estimate the date for each section of the sediment cores as follows: 222

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

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

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

227  $C_i \times r \times \rho_i$ 

where  $C_i$  is the concentration of contaminants ( $\sum PCBs$ ,  $\sum DDTs$ , and  $\sum PAHs$ ) in sediment layer *i* (ng g<sup>-1</sup>), *r* is the SAR in the sediment core (cm y<sup>-1</sup>) and  $\rho_i$  is the bulk dry density of the sediment layer *i* (g cm<sup>-3</sup>).

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:

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

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

246

### 247 **3. Results**

### 248 3.1 Sediment characteristics

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

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

259

### 260 3.2 Organochlorine compounds

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

In the deep southern Adriatic, OCs levels were close to the MQL (0.01 to 0.06 ng g<sup>-1</sup> for PCBs and 0.04 to 0.3 ng g<sup>-1</sup> for DDTs) and were detected in roughly half of the samples. Only PCB congeners 138 and 180 were detected in measurable amounts and their sum ranged between 0.1 and 2.1 ng g<sup>-1</sup> (0.5  $\pm$  0.3 ng g<sup>-1</sup>), and between <DL and 1.4 ng g<sup>-1</sup> (0.3  $\pm$  0.3 ng g<sup>-1</sup>) off the Bari canyon and at the sediment drift (stations 1 and 2), respectively. The  $\Sigma$ DDTs ranged from <DL to 2.1 ng g<sup>-1</sup> (0.6  $\pm$  0.6 ng g<sup>-1</sup>) at station 1 and from <DL to 0.7 ng g<sup>-1</sup> (0.3  $\pm$  0.3 ng g<sup>-1</sup>) 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  $\sum_{16}$ 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, Phe, and An) PAHs was somewhat higher in the sediment taken in the sediment drift 291 292 (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.

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

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 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, 305 respectively) in comparison to the northern Adriatic (0.02 to 2.2 ng cm<sup>2</sup> y<sup>-1</sup>; Table 1). 306 Annual fluxes and concentrations of OCs ( $\sum_{5}$ PCBs and  $\sum_{7}$ DDTs) followed a similar 307 308 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  $\Sigma_5$  PCBs (2.1 ng g<sup>-</sup> <sup>1</sup>, 0.7 ng g<sup>-1</sup>, and 5.2 ng g<sup>-1</sup> in stations 1, 2, and 9) and  $\Sigma$ DDTs (2.1 ng g<sup>-1</sup>, 0.7 ng g<sup>-1</sup>, 312 and 2.5 ng g<sup>-1</sup> in stations 1, 2, and 9, respectively). After the 1980s, annual fluxes and 313 314 concentrations of OCs decreased upwards until recent sediments, where PCBs presented concentrations of 0.5 ng  $g^{-1}$ , <LQ, and 2.7 ng  $g^{-1}$  and DDT presented concentrations of 315 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), 316 317 and 9 (Po river prodelta), respectively.

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

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

330

331 3.5 Ecological Risk Assessment

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

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343 4.1. Levels of OCs and PAHs in sediments

Few studies have reported the temporal distribution of organic contaminants along the 344 345 Adriatic Sea. PAHs levels detected in the Po River prodelta in our study were slightly higher when compared to those previously detected in the same area (102 to 346 ng  $g^{-1}$ ; 346 347 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 slightly higher than previously reported (<DL-0.2 ng g<sup>-1</sup> for  $\Sigma_5$ PCBs; Combi et al., 350 351 2016).

PAH concentrations in our study were lower in comparison to those reported in 352 353 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., 2017). While PAH levels in the Po river prodelta were higher in comparison to less-355 356 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 indicate that the process of on-land weathering tends to favor the formation and 373 374 preservation of DDE, as compared to DDD (Zhang et al., 2002).

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

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

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

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

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 sever typhus epidemics affecting the civilians and military personnel in 1943-412 1944 (Wheeler, 1946; Soper at 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).

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

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 beginning of the 1900s). This finding is consistent with the relatively low consumption 429 430 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 station, and at the beginning of the 1980s for  $\Sigma$ DDT and  $\Sigma$ PAH in the South-Western 443 444 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, the latter increases until the middle of the 20<sup>th</sup> century (Figure S3 from Supplementary 449 450 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). Although natural gas was used since the end of the 19<sup>th</sup> century, it surpassed the use of 459 coal in the 1970s (Malanima, 2006). In turn, relative proportions of HMW PAHs 460 461 showed a slight decrease specially after the 1980's. In this period, the consumption of natural gas was still growing while the consumption of oil showed and important 462 463 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).

Contaminants deposition in the Po River prodelta (station 9) is influenced by episodic 467 468 flood sedimentation (Palinkas and Nittrouer, 2007) (Figure 4). During the XX century, several flooding events with daily peak discharge above 8,000 m<sup>3</sup>s<sup>-1</sup> occurred, 469 470 specifically in 1926, 1928, 1951, 1976, 1994 and 2000, with the absolute maximum daily discharge observed on 20 May 1926 (9,780 m<sup>3</sup> s<sup>-1</sup>; Zanchettin et al., 2008). ΣPAH, 471 472  $\Sigma$ PAH,  $\Sigma$ DDT 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 (ARPA, 2014), a peak daily discharge of 8940 m<sup>3</sup>s<sup>-1</sup> was registered during a major flood 474 475 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 mean daily maximum water discharge above  $9,000 \text{ m}^3\text{s}^{-1}$  as well as the longest duration 479 of high river discharge (> 4,000  $\text{m}^3\text{s}^{-1}$ ) (Tesi et al., 2008). The signature of this flood 480 event is clearly marked by the concurrent heaviest  $\delta^{13}C$  signal, indicating the 481 482 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 secondary sources inputs. This pattern is consistent with the marked d<sup>13</sup>C terrigenous 492 493 (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 the500 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:

a) Concentrations of PCBs and DDTs present a decreasing trend in sediment cores
from the Western Adriatic Sea after the 1980s due to international restrictions
and national regulations, and their deposition matched their historical use in
Italy in agreement with consumption and accumulation patterns detected in other
regions and countries of the world;

- b) The vertical profiles of PAHs seem to reflect the shifts in contamination sources
  along the sediment cores, which is ultimately related to historical energy
  production and consumption in Italy;
- c) Sedimentary PAHs in the western Adriatic Sea are a mixture of combustion
  related emissions among which LMW, more susceptible to degradation
  processes, represent a minor fraction of the detected compounds. PAHs related
  to emissions from coal or biomass combustion show higher abundances in the
  bottom of the sediment cores (up to the ~1940s), while the abundance of PAHs

		Journal Fre-proof
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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**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<sup>-2</sup> y<sup>-1</sup>) for the sediment cores from the Bari canyon (station 1), sediment Drift (station 2), and Po River prodelta (station 9).

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

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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></dl- 	This study
Dauno seamount	1880- 2014	11-49 <sup>a</sup>	<dl- 2.1<sup>g</sup></dl- 	<dl- 0.7<sup>m</sup></dl- 	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>	-0	Combi et al. (2016)
Gondola slide (southern Adriatic)	1894- 2007	-	<dl- 0.2<sup>g</sup></dl- 	0-	Combi et al. (2016)
Northwest coast of Spain	1950- 2011	49.6- 2489 <sup>d</sup>	0	<u> </u>	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°</dl- 	Cai et al. (2016)
Gulf of Thailand	1940- 2004	10-120 <sup>f</sup>	<dl- 2.3<sup>k</sup></dl- 	-	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></dl- 	-	-	Martins et al. (2010)
2	1931- 2006	-	<dl- 11.9<sup>1</sup></dl- 	-	Combi et al. (2017)

**Table 2.** Comparison of total PAH, PCB and DDT concentrations (in ng  $g^{-1}$  dry weight)

<sup>a</sup>:  $\sum_{16}$ PAHs; <sup>b</sup>:  $\sum_{12}$ PAHs; <sup>c</sup>:  $\sum_{10}$ PAHs; <sup>d</sup>:  $\sum_{35}$ PAHs; <sup>e</sup>:  $\sum_{15}$ PAHs; <sup>f</sup>:  $\sum_{18}$ PAHs <sup>g</sup>:  $\sum_{5}$ PCBs; <sup>h</sup>: not informed; <sup>1</sup>:  $\sum_{127}$ PCBs; <sup>J</sup>:  $\sum_{20}$ PCBs; <sup>k</sup>:  $\sum_{24}$ PCBs; <sup>I</sup>:  $\sum_{7}$ PCBs <sup>m</sup>:  $\sum_{p,p'}$ -DDT, p,p'-DDD, p,p'-DDE; <sup>n</sup>: DDE; <sup>o</sup>:  $\sum_{p,p'}$ -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.



- **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

- 11 (station 2) on deep South-Western Adriatic Margin (SWAM). Circles represent contaminant concentrations
- $(ng g^{-1})$  and triangles represent contaminant fluxes  $(ng cm^2 y^{-1})$ .



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



**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<sub>org</sub>) 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

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### **Declaration of interests**

 $\boxtimes$  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:

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