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Distribution and fate of legacy and emerging contaminants along the Adriatic Sea: A comparative study

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1 **Distribution and fate of legacy and emerging contaminants along the Adriatic Sea:**  
2 **a comparative study**

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16

17

18 **Abstract**

19 The spatial distributions and fates of selected legacy and emerging compounds were  
20 investigated and compared in surface sediments sampled along the Adriatic mud-wedge  
21 and in deep-sea regions from the southern Adriatic basin. Results indicated that the  
22 concentrations of legacy contaminants (PAHs, PCBs and DDTs) and emerging  
23 contaminants (tonalide, galaxolide, EHMC, octocrylene, BP3 and NP) ranged from 0.1  
24 to 572 ng g<sup>-1</sup> and from <LOD to 40.7 ng g<sup>-1</sup>, respectively. In general, higher  
25 concentrations and estimated burdens were detected in the northern Adriatic,  
26 highlighting the importance of the Po River as the major contributor for the inputs of  
27 legacy and emerging contaminants to sediments in the Adriatic Sea. Nevertheless, the  
28 prevalence of some UV filters and fragrances in the central and southern Adriatic  
29 indicates that the proximity to tourist areas and WWTPs discharges seems to affect the  
30 distribution of those compounds. The accumulation of contaminants in the deep-sea  
31 areas supports the inference that this region may act as an important repository for  
32 contaminants within the Adriatic Sea. Estimated annual contaminant accumulation  
33 reveals that both, legacy and emerging contaminants accumulate preferentially in the  
34 northern Adriatic (40 to 60% of the total annual contaminant accumulation), where the  
35 presence of legacy, and to a lesser extent emerging contaminants, are likely to pose an  
36 immediate or long-term hazard to resident biota.

37

38 **Keywords:** emerging contaminants, Adriatic mud-wedge, hazard quotients, total mass,  
39 contaminant accumulation

40 **Capsule**

41

42 Legacy and emerging contaminants accumulate preferentially in the northern Adriatic.

43 Large-scale circulation transfers sediment-bound contaminants to deep-sea regions in

44 the southern Adriatic.

## 45 **Introduction**

46 There are currently more than 85,000 chemicals in production and use world-wide, a  
47 fraction of which is accumulated in marine and coastal areas through deliberate  
48 dumping, natural runoff from the land or atmospheric deposition (Sahu et al., 2009;  
49 McKnight et al., 2015). Therefore, there is a growing concern over the last decades  
50 about the environmental distribution and the potential effects of these synthetic  
51 substances. Environmental policies and efforts are being made at different levels in  
52 order to achieve a comprehensive understanding and protection of marine systems. For  
53 instance, the Marine Strategy Framework Directive (MSFD) has been adopted at  
54 European level in order to achieve Good Environmental Status (GES) of the EU's  
55 marine waters by 2020, addressing data availability, knowledge gaps and research  
56 priorities regarding contaminants and marine pollution impacts (2008/56/EC; European  
57 Commission, 2008).

58 Persistent organic pollutants (POPs; e.g. polychlorinated biphenyls - PCBs, polycyclic  
59 aromatic hydrocarbons – PAHs, and chlorinated pesticides) are a well-known group of  
60 legacy contaminants, which have been monitored and regulated in most parts of the  
61 world for the last four decades, being also referred as “regulated contaminants” (Jones  
62 and de Voogt, 1999; Lohmann et al., 2007). On the other hand, emerging contaminants  
63 (ECs) are chemical compounds that are not necessarily new, but are not or are only  
64 partly regulated and are not included in routine monitoring programs (Pintado-Herrera  
65 et al., 2016a).

66 Despite the availability of an important amount of data sets and long time-series for  
67 legacy contaminants, most of the data available refers to restricted areas and a shortage  
68 of off-shore datasets has been detected (Crise et al., 2015). Regarding emerging  
69 contaminants, although they have been increasingly studied in water, including drinking  
70 water, rivers, groundwater, wastewaters and effluents from wastewater treatment plants  
71 (WWTPs) since the 1990's (Tijani et al., 2015 and references therein), studies focusing  
72 on the fate of emerging contaminants in the marine environment are rather scarce and  
73 the knowledge on their occurrence, fate and effects is still limited (Beretta et al., 2014).

74 As POPs and some groups of ECs sorb preferentially to suspended particulate matter,  
75 sequestration by sinking particles and burial in deep ocean sediment may represent a  
76 major sink for lipophilic contaminants (Dachs et al., 2002; Desforges et al., 2014; Sobek  
77 and Gustafsson, 2014). Concerning the Adriatic Sea, previous studies have suggested

78 that the ultimate repository for contaminants are deep-sea areas located in the southern  
79 Adriatic where the cascading of the North Adriatic Dense Water (NAdDW) is able to  
80 quickly transfer suspended particles and, therefore, particle-binding contaminants,  
81 coming from the north Adriatic (Turchetto et al., 2007; Tesi et al., 2008; Combi et al.,  
82 2016; Langone et al., 2016).

83 Thus, the aim of this work was to investigate and compare levels and spatial patterns of  
84 selected groups of regulated and emerging contaminants in sediments from coastal and  
85 deep-sea areas in the Adriatic Sea in order to fully characterize the transfer and burdens  
86 of contaminants from coastal waters to the open sea along the Adriatic margin. We also  
87 aim to contribute with unprecedented data on the presence of emerging contaminants in  
88 the Adriatic Sea, filling the gap of information on the occurrence and off-shore levels of  
89 these substances. .

90

## 91 **Material and methods**

92

### 93 *Study area*

94 The Adriatic Sea (Figure 1) is a shallow semi-enclosed basin in Southern Europe. The  
95 Adriatic Sea is commonly divided into three sub-basins: the northern Adriatic, at the  
96 north of Ancona and with depths up to 100 m; the middle Adriatic, between Ancona and  
97 the Gargano Promontory, reaching depths of 270 m; and the southern Adriatic, from the  
98 Pelagosa Sill to the Otranto Strait, which includes the deepest area of the Adriatic Sea  
99 (the South Adriatic Pit, up to 1200m).

100 Freshwater input comes mainly from the Po River (northern Adriatic), which is  
101 responsible for the transport of approximately one-fourth of the sediment that enters the  
102 Adriatic Sea (Frignani et al., 2005). The remaining material is supplied by northern  
103 rivers draining the eastern and short, steep rivers draining the Apennine Mountains  
104 (Frignani et al., 2005). As a result of thermohaline factors and water dynamics, the  
105 material is exported southwards and the suspended material accumulates in a continuous  
106 belt along the coast, forming the late-Holocene mud wedge (Correggiari et al., 2001;  
107 Cattaneo et al., 2003).

108 During cold and dry winters, the northern Adriatic is subject to intense cooling  
109 associated with local wind forcing (Bora wind), resulting in the formation of the  
110 NAdDW, the densest water of the whole Mediterranean (Vilibić and Supić, 2005; Tesi  
111 et al., 2008). After its formation, the NAdDW spreads southwards, sinking along the  
112 bathymetric gradient and reaching deep regions from the southern Adriatic basin by a  
113 process of dense water cascading (Tesi et al., 2008; Chiggiato et al., 2016; Langone et  
114 al., 2016). The cascading of the NAdDW is responsible for the higher particle delivery  
115 in the southern Adriatic, playing a first order control on the particulate fluxes through  
116 the south-western Adriatic margin (Turchetto et al., 2007; Langone et al., 2016).

117

### 118 *Sampling and sediment characteristics*

119 The sediment sampling was performed in October 2014 on board the O/V OGS Explora  
120 in transects perpendicular to the coast from Northern to Southern Adriatic (Figure 1).  
121 Surface sediment samples were collected along the Adriatic mud wedge, the Bari  
122 Canyon and the South Adriatic Pit by mini box corer or oceanic box corer. The top 0.5  
123 cm of undisturbed sediment was sampled. Sediments were placed into pre-cleaned glass  
124 jars and stored at -20 °C.

125 Porosity ( $\phi$ ) was calculated from the loss of water between wet and dry sediment  
126 according to equations suggested by Berner (1971), assuming a sediment density of  
127  $2.65 \text{ g cm}^{-3}$  and a water density of  $1.027 \text{ g cm}^{-3}$ . Grain size was determined after a pre-  
128 treatment with  $\text{H}_2\text{O}_2$  and wet sieving at  $63 \mu\text{m}$  to separate sands from fine fractions.  
129 Total nitrogen (TN) content were determined by elemental analysis (EA) of combusted  
130 aliquots with a Fison NA2000 EA, and organic carbon (OC) was measured on  
131 decarbonated samples (1 M HCl).

132

### 133 *Analytical method and instrumental analyses*

134 The legacy and emerging compounds analyzed in the sediment samples, their respective  
135  $\log K_{ow}$ , main applications and sources are presented in Table 1. Sediments were  
136 extracted using an accelerated solvent extraction ASE 200 system (Dionex, USA)  
137 according to the extraction and in-cell clean-up method optimized by Pintado-Herrera et  
138 al. (2016a). Briefly, the extraction cells (11 mL) were prepared with 1 g of activated  
139 alumina (150°C for 16 hours; USEPA method 3610b) and 0.5 g of activated copper



140 powder. Approximately 4 g of air-dried and milled sediment were homogenized with 1g  
141 of alumina and placed into the extraction cells. The extraction procedure consisted of  
142 three static extraction cycles using dichloromethane, where the samples were pre-heated  
143 for 5 minutes and extracted for 5 minutes in each cycle at a temperature of 100°C and a  
144 pressure of 1500 psi. The eluates were evaporated to dryness and re-dissolved in 0.5 mL  
145 of ethyl acetate. The final extracts were centrifuged (10000 rpm for 10 minutes) and  
146 filtered (0.22 µm) to remove possible interferences. The efficiency of the extraction  
147 method was evaluated by using standard reference material (marine sediment 1941b,  
148 National Institute of standards and Technology: NIST) for POPs and by spiking samples  
149 at three different concentrations (20, 100 and 200 ng g<sup>-1</sup>) for ECs. Recovery percentages  
150 were between 70 and 100%. More specific details on this can be found at Pintado-  
151 Herrera et al. (2016a).

152 Separation, identification and quantification of target compounds were performed using  
153 gas chromatography (SCION 456-GC, Bruker) coupled to a triple quadrupole mass  
154 spectrometer equipped with a BR-5ms column (length: 30 m, ID: 0.25 mm, film  
155 thickness: 0.25 µm). The oven temperature was programmed to 70 °C for 3.5 min,  
156 increasing at 25 °C min<sup>-1</sup> to 180 °C, increasing at 10 °C min<sup>-1</sup> to 300 °C, holding this  
157 temperature for 4 min. A derivatizing agent (*N*-(*tert*-butyldimethylsilyl)-*N*-  
158 methyltrifluoroacetamid - MTBSTFA) was added to the samples to improve signal  
159 intensity and peak shape of some target compounds (e.g., BP3). Internal standards  
160 (mixture of deuterated compounds) were also included to account for the matrix  
161 suppression. Calibration curves were prepared for each target compound at different  
162 concentrations (from 5 to 500 ng g<sup>-1</sup>). Target compounds were identified and quantified  
163 by comparison of retention times and two transitions of each analyte (one for  
164 quantification and one for confirmation) of the samples with external standard solutions.  
165 Procedural blanks were performed for each extraction series of 10 samples using  
166 alumina and analyzed in the same way as samples. Method detection limits (MDL) were  
167 determined for each analyte as 3 times the signal to noise ratio in spiked sediment  
168 samples and were between 0.003 and 0.54 ng g<sup>-1</sup> depending on the target compound.

169

170 *Inventories, total burdens, contaminant accumulation and risk assessment*

171 Inventories were calculated for surface sediment using the following equation:

172

$$Inventory = \sum C_i d_i \rho_i$$

173 where  $C_i$  is the concentration of each contaminant in sediment sample  $i$  (ng g<sup>-1</sup> dry  
174 weight),  $d$  is the thickness of the sediment sampled (0.5 cm) and  $\rho_i$  is the dry mass bulk  
175 density (g cm<sup>-3</sup>). In order to calculate the total burdens (mass of contaminants), the  
176 Adriatic Sea has been divided in several boxes defined by different orientation of the  
177 coastline which, along with the general water circulation, controls the variability of  
178 sediment accumulation along the modern Adriatic mud wedge, as suggested by Frignani  
179 et al., 2005 (Figure S1 from Supplementary Material). The total burdens were calculated  
180 by multiplying the mean calculated inventories in surface sediments by the area of the  
181 boxes (Yang et al., 2012). According to the annual sediment accumulation rate (Tg y<sup>-1</sup>)  
182 estimated by Frignani et al (2005), the annual contaminant accumulation (kg y<sup>-1</sup>) for  
183 each box was also estimated.

184 For the preliminary risk assessment, the hazard quotients (HQs) for legacy and  
185 emerging contaminants were calculated using the measured environmental  
186 concentration (MEC) and the predicted non-effect concentration (PNEC), as follows:

187

$$HQ = MEC / PNEC$$

188 The PNEC values were either obtained from available literature or calculated using no  
189 observed effect concentrations (NOEC) from chronic toxicity bioassays or acute toxic  
190 endpoints (half maximal effective concentration, or EC50) and dividing toxicity data by  
191 a factor of 100 or 1000, respectively. Both, PNEC and calculated PNEC values, are  
192 presented in Pintado-Herrera et al. (2016b). Concentrations of target compounds in  
193 surface sediments presented in this work were used as MEC. For interpretation, HQ <  
194 0.1 indicates no hazard, 0.1 < HQ < 1 a low hazard, 1 < HQ >10 a moderate hazard, and  
195 HQ > 10 a high hazard ( Lemly, 1996; Chen et al., 2010).

196

### 197 *Statistical analyses*

198 To explore the relationship between the variables, Pearson's correlation coefficient at  
199 0.05 significance level was applied. Linear discriminant analysis was performed using  
200 the statistical package "MASS" (Venables and Ripley, 2002). Discriminant analysis is a  
201 statistical procedure for identifying boundaries between groups of samples based on  
202 quantitative predictor variables (Mourier et al., 2014). In our case, the variables used

203 were the contaminant concentrations, and the percentage of OC and fine sediments  
204 (mud, as sum of the silt and clay fractions), while the groups were the northern, central,  
205 and southern Adriatic Sea sectors. Data were z-scoring standardized in order to  
206 eliminate the influence of different units and make each determined variable have equal  
207 weighting. Statistical data analyses were performed with R software (R Core Team,  
208 2013).

209

## 210 **Results**

211

### 212 *Sediment characteristics*

213 Fine fractions (silt and clay) were predominant in sampled sediments accounting for  
214 ~50 to ~99% (Table 2 and Tables S1 to S3 from Supplementary Material). OC was  
215 relatively low and limited in variability within the Adriatic mud-wedge sediments,  
216 varying between 0.6 and 1.6%. These levels are consistent with previous data on OC  
217 content found in the region (Tesi et al., 2007, 2013; Turchetto et al., 2007). In general,  
218 OC and C/N ratio were higher in the northern section ( $1.0 \pm 0.2\%$  and  $9.6 \pm 0.8$ ,  
219 respectively), especially in the samples closer to the Po River prodelta. The lowest OC  
220 and C/N values were detected in sediments off coast from central ( $0.5$  to  $0.9\%$  and  $7.6$   
221 to  $9.5$ , respectively) and southern ( $0.5$  to  $0.8\%$  and  $7.7$  to  $9.4$ , respectively) areas.

222

### 223 *Concentrations of contaminants in sediments*

224 Among all target contaminants considered in this study, PAHs were by far the most  
225 prevalent compounds in surface sediments from the Adriatic Sea, with  $\sum_{16}$  PAHs  
226 ranging from  $38.8$  to  $572$  ng g<sup>-1</sup> (Table 2 and Tables S1 to S3 from Supplementary  
227 Material). The highest concentrations (presented as the mean concentration  $\pm$  standard  
228 deviation - SD) were detected in the northern section ( $300 \pm 101$  ng g<sup>-1</sup>), followed by the  
229 central ( $115.3 \pm 27.4$  ng g<sup>-1</sup>) and southern sections ( $107.4 \pm 64.2$  ng g<sup>-1</sup>). High molecular  
230 PAHs (HMW; 4–6 rings) accounted for 65 to 95% of total PAHs. The ratio between  
231 low- and high-molecular weight PAHs (LMW and HMW, respectively) ranged from 0.1  
232 to 0.5, while the ratios between indeno[1,2,3-cd]pyrene and benzo[g,h,i]perylene  
233 (Ip/Ip+Bper), fluoranthene and pyrene (Flt/Pyr and Flt/Flt+Pyr), and benz[a]anthracene

234 and chrysene (Ba/Ba+Chr) ranged from 0.2 to 0.6, from 0.9 to 1.5 and from 0.3 to 0.5,  
235 respectively.

236 UV filters and nonylphenol (NP) were next in terms of concentration after PAHs. They  
237 ranged from <LOD (below limit of detection) to 40.7 ng g<sup>-1</sup>. Octocrylene was the most  
238 abundant UV filter (16.3±9.6 ng g<sup>-1</sup>, 7.6±6 ng g<sup>-1</sup> and 6.8±4 ng g<sup>-1</sup> in the northern,  
239 central and southern sectors, respectively), followed by EHMC (4.5±2.2 ng g<sup>-1</sup>, 2.4±1 ng  
240 g<sup>-1</sup> and 3.2±1.4 ng g<sup>-1</sup> in the northern, central and southern sectors, respectively). Both  
241 compounds were detected in all the sediment samples. Conversely, BP3 was detected at  
242 very low concentrations (0.05±0.05 ng g<sup>-1</sup>, 0.02±0.02 ng g<sup>-1</sup> and 0.06±0.06 ng g<sup>-1</sup> in the  
243 northern, central and southern sectors, respectively) and only in ~50% of the sediment  
244 samples. Regarding NP isomers, their higher concentrations were detected in the  
245 northern sector (17±8.4 ng g<sup>-1</sup>), while the concentrations in the central and southern  
246 sectors were very similar, with mean values of 6.3±4.5 ng g<sup>-1</sup> and 6.7±4.5 ng g<sup>-1</sup>,  
247 respectively.

248 Concentrations of fragrances ranged from <LOD to 24.3 ng g<sup>-1</sup> (Table 2 and Tables S1  
249 to S3 from Supplementary Material). In general, tonalide was present in higher  
250 concentrations (6.2±4.6 ng g<sup>-1</sup>, 2.9±2.2 ng g<sup>-1</sup> and 6.0±2.7 ng g<sup>-1</sup> in the northern, central  
251 and southern sectors of the Adriatic Sea, respectively) in the sediment samples in  
252 comparison to galaxolide (4.3±2.8 ng g<sup>-1</sup>, 1.9±1.5 ng g<sup>-1</sup> and 4.0±2.7 ng g<sup>-1</sup> in the  
253 northern, central and southern sectors, respectively; Table 2). Galaxolide to tonalide  
254 ratios ranged from 0 to 5.4 (1±0.9).

255 Lastly, the organochlorine compounds (PCBs and DDTs) were detected at the lowest  
256 concentrations and presented a similar range of concentrations. Total PCBs ( $\Sigma_5$ PCBs)  
257 and total DDTs (*p,p'*DDD, *p,p'*DDE and *p,p'*DDT) in surface sediments varied between  
258 0.05 and 4.2 ng g<sup>-1</sup> and between 0.05 and 4.3 ng g<sup>-1</sup> respectively (Table 2 and Tables S1  
259 to S3 from Supplementary Material). Similarly to the rest of target compounds, they  
260 were also detected in higher concentrations in the northern box (2.0±0.9 ng g<sup>-1</sup>)  
261 followed by the middle (0.7±0.4 ng g<sup>-1</sup>) and southern (0.4±0.3 ng g<sup>-1</sup>) boxes. Although  
262 total DDTs were also higher in the northern sector (1.6±1.0 ng g<sup>-1</sup>), they were very  
263 similar between the central and southern boxes (0.6±0.2 and 0.7±0.3 ng g<sup>-1</sup>,  
264 respectively). While DDE and DDD were ubiquitous in sediments from the Adriatic  
265 Sea, DDT was detected only in 20% of the samples.

266

267 *Inventories, total burdens and contaminant accumulation*

268 The estimated inventories, burdens and contaminant accumulation in the Adriatic Sea  
269 are presented in Table 2. As expected from concentration data, PAHs ( $\sum_{16}\text{PAHs}$ )  
270 presented the highest inventories (mean value and SD of  $810\pm 380\text{ ng cm}^{-2}$  among the  
271 three sectors), followed by octocrylene and NP ( $47\pm 19\text{ ng cm}^{-2}$  and  $46\pm 20\text{ ng cm}^{-2}$ ,  
272 respectively). The total inventories of the organochlorine compounds were very similar,  
273 with  $4.8\pm 3\text{ ng cm}^{-2}$  and  $4.5\pm 2\text{ ng cm}^{-2}$  for PCBs ( $\sum_5\text{PCBs}$ ) and DDTs ( $\sum p,p'$ -DDT,  $p,p'$ -  
274 DDD and  $p,p'$ -DDE), respectively. The mean inventory of the fragrances was  
275 approximately  $15\pm 4\text{ ng cm}^{-2}$  for galaxolide and  $22.5\pm 5.5\text{ ng cm}^{-2}$  for tonalide. Regarding  
276 the other UV filters, EHMC presented a mean inventory of  $16\pm 4.5\text{ ng cm}^{-2}$  and BP3 of  
277  $0.2\pm 0.1\text{ ng cm}^{-2}$ . Estimated burdens in the whole Adriatic basin were nearly 15,000 kg  
278 for PAHs, 900 kg for octocrylene, 765 kg for NP, 424 kg for tonalide, 330 kg for  
279 EHMC, 275 kg for galaxolide, 80 kg for PCB and DDT, and 4 kg for BP3. Total annual  
280 contaminant accumulation in the Adriatic Sea ranged from 0.2 for BP3  $\text{kg y}^{-1}$  to  $\sim 7800$   
281 for PAHs  $\text{kg y}^{-1}$ . The total annual accumulations were similar for NP and octocrylene  
282 ( $\sim 450\text{ kg y}^{-1}$ ) and the organochlorine compounds ( $\sim 45\text{ kg y}^{-1}$ ). EHMC, galaxolide and  
283 tonalide presented similar total annual accumulation as well ( $\sim 140$  to  $210\text{ kg y}^{-1}$ ).

284

285 **Discussion**

286

287 *Comparison of the occurrence, sources and distribuion of legacy and emerging*  
288 *contaminants in sediments*

289 Figure 2 illustrates the occurrence of emerging contaminants in sediments from  
290 transition and coastal areas around the world, including our sampling area (Adriatic  
291 Sea). So far, only a few studies have reported the levels of emerging contaminants in  
292 sediments, especially in marine and deep-sea ecosystems. In comparison to the Po  
293 River, the fragrances tonalide and galaxolide and the endocrine disruptor NP presented  
294 far lower mean concentrations in our study (Viganò et al., 2015). Overall, NP  
295 concentrations were far lower in comparison to other areas, except for coastal areas in  
296 southern France (Hong et al., 2009). Tonalide and galaxolide levels were also lower  
297 when compared to semi-enclosed coastal areas such as Cádiz Bay (Pintado-Herrera et

298 al., 2016a) and Hempstead Bay (Fisher et al., 2016), but comparable to the levels  
299 reported in urbanized coastal areas from China (Pintado-Herrera et al., 2016b) and  
300 Korea (Lee et al., 2014). The concentrations of the UV filters EHMC and octocrylene in  
301 our study were far lower than those reported in the Eastern Mediterranean (Amine et al.,  
302 2012), while EHMC presented similar concentrations to those detected in touristic  
303 areas, as southern France (northwestern Mediterranean coast; Amine et al., 2012) and  
304 urbanized areas, as the Pearl River Estuary, China (Pintado-Herrera et al., 2016b).

305 More detailed information on the concentrations and spatial trends of target  
306 contaminants in the Adriatic Sea is presented in Figures S2 to S6 from Supplementary  
307 Material and revealed a similar pattern, with decreasing concentrations from the Po  
308 River prodelta southward to the Otranto channel and in deep areas from the South-  
309 Western Adriatic Margin (SWAM). The Po River is the largest and most important  
310 Italian river, draining large agricultural and highly industrialized areas, inhabited by  
311 about 15 million of people, and being responsible for the transport of approximately  
312 one-fourth of the sediment that enters the Adriatic Sea (Frignani et al., 2005; Romano et  
313 al., 2013; Tesi et al., 2007). Thus, the Po River appears to be the major contributor for  
314 the inputs of legacy and emerging contaminants to sediments in the Adriatic Sea.

315 Although contaminant concentrations are generally lower in the central and southern  
316 sectors, some increased concentrations can be noticed especially around Ancona and  
317 Bari, which are areas with intense human activities, sheltering two of the most  
318 important commercial and passenger harbors of the Adriatic Sea (Mali et al., 2015), that  
319 are local sources of contaminants. PAHs and PCBs have been previously detected at  
320 higher concentrations in these areas, especially around the Bari port (Guzzella and  
321 Paolis, 1994; Mali et al., 2015; Combi et al., 2016). As to the fragrances, their  
322 application in a broad range of personal care products, including soaps and detergents  
323 (OSPAR Commission, 2004), may help explaining their presence in these areas.  
324 Fragrances and UV filters also presented somewhat higher levels in touristic coastal  
325 areas in the central and southern Adriatic, which may be related to the direct input from  
326 recreational activities (bathing, swimming) (Pintado-herrera et al., 2016b). Additionally,  
327 the proximity to major cities (e.g. Ancona and Bari) and tourist facilities results in an  
328 increased load of ECs from WWTPs effluents, which, in turn, represent one of their  
329 major sources to the marine environment (Chase et al., 2012; Villa et al., 2012).  
330 Previous studies also related the presence of fragrances and UV filters to both the

331 proximity to tourist areas and WWTPs discharges (Downs et al., 2015; Villa et al.,  
332 2012).

333 Both, legacy and emerging contaminants were also detected in deep sediments within  
334 the SWAM. Although the contaminant contents are not at hazardous levels, the  
335 detection of highly chlorinated PCBs (Combi et al., 2016) and other highly hydrophobic  
336 compounds (e.g. octocrylene and benzo[g,h,i]perylene) reinforces the hypothesis that  
337 the cascading of the NAdDW would be able to transfer particle-binding contaminants  
338 coming from the north Adriatic and testifies that the impact of anthropic contamination  
339 by inland inputs may not be confined to the proximity of the river mouths but can be  
340 exported at long distance (600 km in the Adriatic) and toward the deep ocean (down to  
341 1200 m).

342 Statistical analysis of the data reveals that concentrations of both legacy and emerging  
343 contaminants (PAHs, PCBs, DDTs and NP) were positively correlated to OC ( $r \geq 0.5$ ;  $p$   
344 value  $\leq 0.01$ ), suggesting that their spatial distribution is dependent on the OC content  
345 of sediments. NP was strongly correlated to legacy contaminants ( $r \geq 0.6$ ;  $p$  value  $<$   
346 0.001) and the UV filters (EHMC and octocrylene) were also correlated ( $r = 0.5$ ;  $p$   
347 value  $< 0.001$ ), confirming these compounds present similar spatial distribution and  
348 may derive from similar input sources. The discriminant analysis explained the data  
349 variance (83.3% and 16.7% for LD1 and LD2). The scatterplot of the two discriminant  
350 functions (LD1 and LD2) shows that the north sector is better separated than the center  
351 and south (Figure 3) and PCBs, PAHs, EHMC and OC were the variables that most  
352 contributed to the group differentiation. According to the confusion matrix, which  
353 evaluates the consistency of classification of samples into groups (Mourier et al., 2014),  
354 the accuracy of the classification appears to be relatively high, since 70%, 80% and 90%  
355 of the samples were well reclassified within the predefined groups (central, southern  
356 and northern areas, respectively). Although PCBs, PAHs, and EHMC were the  
357 compounds of highest importance for separating the areas, the stronger discrimination  
358 of the northern sector can be also related to the higher concentrations detected for most  
359 contaminants in this area, especially close to the Po River prodelta. On the other hand,  
360 the spatial distribution of ECs was generally not as clear as the distribution detected for  
361 legacy contaminants, especially in the central and southern Adriatic, which may explain  
362 the weak differentiation among these groups.

363 A more detailed analysis of each class of contaminants shows different compositional  
364 patterns. Regarding legacy contaminants, the Adriatic Sea sediments were depleted in  
365 LMW (2–3 rings) and enriched in HMW (4–6 rings) PAHs (Tables S1 to S3 from  
366 Supplementary Material), and Ip/Ip+Bper, Flt/Pyr, Flt/Flt+Pyr and Ba/Ba+Chr ratios  
367 indicate PAHs sources from biomass and petroleum combustion (Figure S7 from  
368 Supplementary Material). These ratios corroborated the pyrolytic origin of PAHs in the  
369 sediment samples from the Adriatic Sea, which is in agreement with previous research  
370 accomplished in the Adriatic Sea (Magi et al., 2002). Considering the organochlorine  
371 compounds, the most abundant PCB congeners were PCB 138 followed by PCB 180,  
372 while among compounds of DDT family, DDE was the prevalent isomer. Although  
373 PCBs and DDTs have been banned in Italy since the late 1970's (Tolosa et al., 1997;  
374 Binelli and Provini, 2003), these contaminants are still present in recent sediments from  
375 the Adriatic Sea. Indeed, previously contaminated soils around the drainage basin of the  
376 Po River can be slowly released over time and seem to be continuously contaminating  
377 waterbodies in the north of Italy, ultimately accumulating in the Adriatic Sea sediments  
378 (Frignani et al., 2004; Combi et al., 2016).

379 Different ratios could be also established for emerging contaminants such as fragrances.  
380 Galaxolide is commercially the most used polycyclic musk fragrance, followed by  
381 tonalide (Villa et al., 2012). In 2000, the production of galaxolide and tonalide in  
382 Europe was estimated on 1427 tonnes and 358 tonnes, respectively (OSPAR  
383 Commission, 2004). For this reason, galaxolide is usually detected in higher  
384 concentrations in continental, marine and transitional ecosystems, as well as in  
385 wastewaters (Chase et al., 2012; Pintado-Herrera et al., 2016a; Sumner et al., 2010).  
386 However, tonalide was found in relatively higher levels than galaxolide in Adriatic Sea,  
387 presenting galaxolide to tonalide ratios in general lower than the commercial ratio of  
388 about 4:1 (OSPAR Commission, 2004). Although both compounds present similar  
389 physico-chemical properties (e.g., log  $K_{ow}$  5.7-5.9 and vapor pressure 0.068 – 0.073;  
390 Chase et al., 2012), previous studies suggested that galaxolide is degraded more easily  
391 than tonalide (Lee et al., 2014), and that tonalide preferentially adsorbs to particulate  
392 matter (Dsikowitzky et al., 2002), which are the most likely reasons why tonalide is  
393 ubiquitous in the Adriatic Sea sediments. Tonalide has also been detected in higher  
394 concentrations in some of the sediment samples from the Po River (Viganò et al., 2015)  
395 and Sacca di Goro Lagoon (Casatta et al., 2015).



396 Octocrylene was the predominant UV filter, followed by EHMC and BP3. Octocrylene  
397 is one of the most used UV filters in Europe, being present in over 80% of sunscreen  
398 products, while EHMC and BP3 can be found, respectively, in ~50% and ~20% of the  
399 products (De Groot and Roberts, 2014; Rastogi, 2002). The octanol-water partition  
400 coefficient is an indicator of the environmental fate of the UV-filters, translating how  
401 they are distributed between sediments/lipids and the aqueous phase (Ramos et al.,  
402 2015). Octocrylene is nowadays of great concern since it is a highly lipophilic  
403 compound, stable, and resistant to sunlight degradation (Gago-Ferrero et al., 2013).  
404 EHMC is also a very hydrophobic compound while BP3 is slightly soluble in water  
405 (Table 1), making it less likely to be encountered in marine sediments.

406 NP isomers presented the highest concentrations among the emerging contaminants  
407 analyzed in our work. NP is an endocrine disrupting compound frequently detected in  
408 high concentrations in continental, marine and transitional waters (Pojana et al., 2007;  
409 Lara-Martín et al., 2014; Meffe and de Bustamante, 2014). Surfactants are among the  
410 most produced and consumed substances in the world and, among their degradation  
411 products, nonylphenol presents hydrophobic properties causing a preferential  
412 accumulation in sediments (Pintado-Herrera et al., 2016a; Pojana et al., 2007). High  
413 concentrations of NP in comparison to other classes of contaminants in sediments from  
414 Venice lagoon (47 – 192 ng g<sup>-1</sup>) have been attributed to the proximity to municipal and  
415 industrial wastewaters treatment plants (Pojana et al., 2007).

416 Fragrances, UV filters and NP can be found in relevant concentrations in both, influent  
417 and effluent wastewaters, as most WWTPs are not designed to treat these types of  
418 substances (Chase et al., 2012; Langford et al., 2015). Because of their hydrophobic  
419 properties, the removal of emerging compounds during wastewater treatment is mainly  
420 related to their sorption on sludge solids (Carballa et al., 2004; Langford et al., 2015).  
421 For instance, the removal efficiency of NP after wastewater treatments is around 50 –  
422 80% (Melo-Guimarães et al., 2013; Stasinakis et al., 2013), while the removal  
423 efficiency of tonalide and galaxolide can be around 85% (Carballa et al., 2004).  
424 Consequently, a significant fraction of emerging compounds is constantly discharged  
425 through WWTPs and untreated wastewater into the aquatic environment, leading to a  
426 widespread contamination of continental, transitional and marine waters (Chase et al.,  
427 2012; Sumner et al., 2010; Villa et al., 2012). Because of their hydrophobic properties,

428 most of these compounds are sorbed to some extent on suspended solids during  
429 wastewater treatment and as a result they can also be found in sludge.

430

431 *Burden estimation, contaminant accumulation, and preliminary risk assessment*

432 Inventories and burden estimations represent the integrated mass of the compounds of  
433 interest and can be used as a tool to understand a suitable insight for further behavior of  
434 the compounds per unit area (Kim et al., 2008; Song et al., 2004). Inventories and total  
435 burdens (total mass of contaminants) were calculated with reference to the top 0.5-cm of  
436 sediment, which means that the actual inventories and total burdens would be much  
437 larger than estimated for the Adriatic Sea. Legacy contaminants presented the highest  
438 total burdens in the northern sector (40-45%) of the Adriatic Sea, while the total  
439 burdens of BP3 and the fragrances were higher in the southern sector (45-50%).  
440 Estimated burdens in the southern Adriatic are especially influenced by the larger total  
441 area in the deep-sea in comparison to the coastal areas (Figure S1 from Supplementary  
442 Material). Total burdens in the central Adriatic ranged from 20 to 40%, with the highest  
443 values corresponding to NP and octocrylene. The similar burdens between the central  
444 and southern sectors reinforces the weak separation detected by the discriminant  
445 analysis and the presence of local sources in these areas.

446 Estimated annual contaminant accumulation highlights that legacy and emerging  
447 contaminants accumulate preferentially in the northern Adriatic (40 to 60% of the total  
448 annual contaminant accumulation), followed by the central (25 to 38%) and southern  
449 Adriatic (8 to 30%). Altogether ~ 12% of the legacy and emerging contaminants  
450 annually entering the Adriatic Sea accumulate in the deep Adriatic basin, which has  
451 been previously suggested to be an additional repository for sediments (Frignani et al.,  
452 2005; Turchetto et al., 2007; Langone et al., 2016). The annual contaminant  
453 accumulation and burden estimation are in agreement with the spatial distribution trends  
454 of legacy and emerging contaminants along the Adriatic Sea, corroborating the  
455 hypothesis that the Po River represents the major input sources of most contaminants to  
456 the Adriatic Sea.

457 In order to estimate and evaluate potential ecotoxicological risks of these chemicals in  
458 sediments from the Adriatic Sea, we calculated the hazard quotients (HQs) for  
459 individual legacy and emerging contaminants (Table S4). Emerging contaminants

460 present no significant ecological risk in sediments of the Adriatic Sea except for the UV  
461 filter EHMC, which poses moderate risk for sediment-associated biota. The HQs  
462 suggested a high risk of adverse effects to biota related to total PAHs, *p,p'*-DDE and  
463 PCBs in the northern sector and related to dibenzo[*a,h*]anthracene and *p,p'*-DDE in the  
464 central and southern sectors. In any case, it is necessary to consider that environmental  
465 matrices contaminated with diverse groups of pollutants are complex in terms of  
466 understanding the interaction mechanisms among different compounds; previous studies  
467 have demonstrated that the presence of many chemicals may have additive  
468 toxicological effect (Cristale et al., 2013).

469 Individual HQs were combined and divided by the number of HQs, similarly to the  
470 approach proposed by Long et al. (2006) for the assessment of mean Sediment Quality  
471 Guidelines (SQGs), in order to investigate the overall risk of contaminants in sediments  
472 from the Adriatic Sea. The combined HQs (~3 and ~4, respectively) for central and  
473 southern Adriatic Sea suggest a moderate hazard for sediment-associated biota, while in  
474 the northern Adriatic section combined HQ suggests high ecotoxicological hazard (HQ  
475 = ~10). Along with the fact that individual HQs suggested high ecotoxicological risk  
476 for organisms for several legacy compounds, we can infer that legacy, and to a lesser  
477 extent emerging contaminants present in sediments from the northern Adriatic Sea are  
478 likely to pose an immediate or long-term hazard to resident biota. In any case, more  
479 specific data on the toxicity of emerging contaminants over marine species is needed to  
480 refine further environmental risk assessments on UV filters, fragrances and many other  
481 new chemicals.

482

### 483 **Conclusions**

484 Emerging and legacy contaminants were investigated in surface sediments along the  
485 modern Adriatic mud wedge and in selected deep-sea areas from the South-Western  
486 Adriatic Margin (SWAM). To the best of our knowledge, this is the first study on ECs  
487 occurrence, levels and distribution at an oceanic basin scale. Spatial trends of legacy  
488 and emerging contaminants revealed a similar pattern, with decreasing concentrations  
489 from the Po River prodelta southward, suggesting the Po River as the major contributor  
490 of contaminants to sediments in the Adriatic Sea. This inference is further corroborated  
491 by the distribution patterns for OC and annual contaminant accumulation along the  
492 Adriatic Sea, with higher values consistently detected in the northern section. A

493 significant presence of emerging compounds has been detected in the southern Adriatic,  
494 especially fragrances and UV filters, most likely related to diffuse sources (e.g. tourist  
495 activities and WWTPs discharges).

496 The hypothesis that the deep-sea areas in the southern Adriatic may represent the final  
497 repository for contaminants entering this system has been reinforced by the annual  
498 contaminant accumulation estimated for this basin. The transfer of contaminants from  
499 coastal waters to the open sea has been related to the cascading of the North Adriatic  
500 Dense Water (NAdDW) in deep-sea areas in the southern Adriatic, which would be able  
501 to quickly transport suspended sediments (and, therefore, particle-binding  
502 contaminants) during these episodic events. Further studies on the occurrence,  
503 distribution and fate of ECs in off-shore aquatic settings and at different latitudes are  
504 encouraged to achieve a better understanding on their environmental behavior on a  
505 global scale.

506

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518

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