

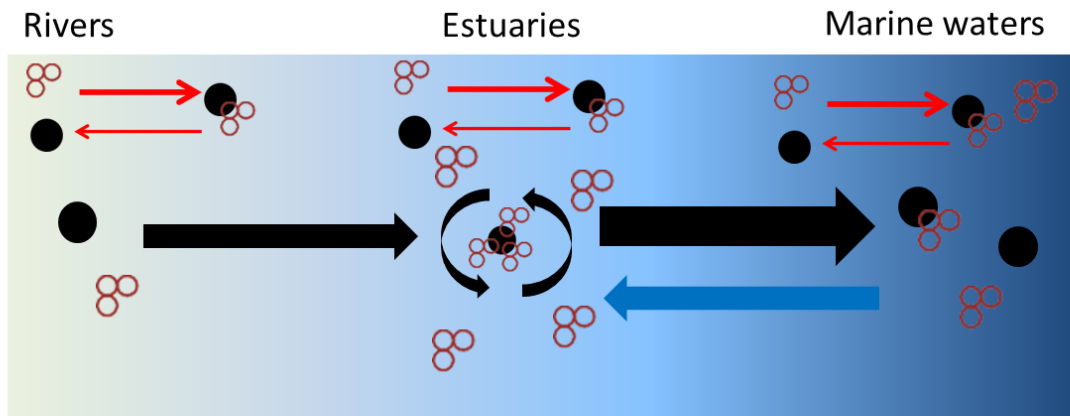


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**Graphical abstract**

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***Salinity range investigated (%)***

**→** Transport riverine to marine waters

**←** Transport marine to estuaries

Microplastic ●

POP ○○

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## Abstract

38 Microplastics represent an increasing source of anthropogenic contamination in aquatic  
39 environments, where they may also act as scavengers and transporters of persistent organic  
40 pollutants. As estuaries are amongst the most productive aquatic systems, it is important to  
41 understand sorption behaviour and transport of persistent organic pollutants (POPs) by  
42 microplastics along estuarine gradients. The effects of salinity sorption equilibrium kinetics  
43 on the distribution coefficients ( $K_d$ ) of phenanthrene (Phe) and 4,4'-DDT, onto  
44 polyvinylchloride (PVC) and onto polyethylene (PE) were therefore investigated. A salinity  
45 gradient representing freshwater, estuarine and marine conditions, with salinities  
46 corresponding to 0 (MilliQ water, 690  $\mu\text{S}/\text{cm}$ ), 8.8, 17.5, 26.3 and 35 was used. Salinity had  
47 no significant effect on the time required to reach equilibrium onto PVC or PE and neither  
48 did it affect desorption rates of contaminants from plastics. Although salinity had no effect on  
49 sorption capacity of Phe onto plastics, a slight decrease in sorption capacity was observed for  
50 DDT with salinity. Salinity had little effect on sorption behaviour and POP/plastic  
51 combination was shown to be a more important factor. Transport of Phe and DDT from  
52 riverine to brackish and marine waters by plastic is therefore likely to be much more  
53 dependent on the aqueous POP concentration than on salinity. The physical characteristics of  
54 the polymer and local environmental conditions (e.g. plastic density, particle residence time  
55 in estuaries) will affect the physical transport of contaminated plastics. A transport model of  
56 POPs by microplastics under estuarine conditions is proposed. Transport of Phe and DDT by  
57 PVC and PE from fresh and brackish water toward fully marine conditions was the most  
58 likely net direction for contaminant transport and followed the order: Phe-PE  $\gg$  DDT-PVC =  
59 DDT-PE  $\gg$  Phe-PVC.

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## Introduction

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Plastics are considered essential in our everyday lives and are used in a wide range of applications, from food packaging, renewable energy and medical devices. World production was 265 million tonnes in 2010, of which 57 million tonnes was produced in Europe (The plastic industry, 2011). The increasing demand for plastics, their low cost of production and high availability mean that end-of-life plastics are accumulating in the environment. The majority of plastic marine litter is believed to come from land-based sources (Sheavly, 2005). The degradation rate of plastic debris in the environment is slow and results in production of small fragments and microplastics. Degradation into small plastic fragments represents an indirect source of microplastics (Barnes et al., 2009; Sivan, 2011) which can also arise from direct sources such as industrial accidental spillages or the release of microbeads used in cosmetics through wastewaters (Browne et al., 2011; Fendall and Sewell, 2009). There is evidence that the abundance microplastics is increasing in the marine environment (Doyle et al., 2011; Thompson et al., 2004) and are potentially bioavailable to a wide range of organisms, for example via ingestion (Browne et al., 2008; Thompson et al., 2009) which have been reported in populations of commercially important fish (Lusher et al., 2013), crustaceans (Murray and Cowie, 2011) as well as seabirds such as the Northern Fulmar (van Franeker, 1985). Laboratory studies have also confirmed that both filter feeding and deposit feeding invertebrates also ingest microplastics (Thompson et al., 2004; Ward and Shumway, 2004). Relatively little is known on about the physical (Wright et al., 2013) and toxicological effects (Bakir et al., submitted) of ingestion of microplastics. Microplastics can accumulate in the digestive gland of marine bivalves and microplastics (< 9.6 µm) were able to translocate to the haemolymph in the common mussel *Mytilus edulis*, where they persisted for at least 48

85 days (Browne et al., 2008). It has also been suggested that ingestion, retention, egestion and  
86 possible re-ingestion of microplastics present potential mechanisms for the transport of  
87 persistent organic pollutants (POPs), and also for the release of chemical additives from  
88 plastics to organisms (Ryan et al., 1988; Tanaka et al., 2013). This will be dependent on the  
89 nature of the chemical substance involved, the size of the plastic particle and from the  
90 perspective of this study, the surrounding physical and chemical environment.

91 Estuaries are among the most productive marine environments, providing habitats for a wide  
92 diversity of seabirds, fish and mammals and are economically important for the exploitation  
93 of fish and shellfish (Allen et al., 2006). As microplastics can be carried to the sea via rivers,  
94 (Moore et al., 2002) they are likely to be transported to the marine environment via estuaries  
95 with the potential to be ingested by estuarine organisms. There is also potential for  
96 microplastics to be transported back into estuarine habitats from the sea by tidal flow. Short-  
97 term transport potential of POPs by microplastics from estuaries to marine waters is under  
98 investigation in this study as estuaries represent relatively rapidly changing physical  
99 environments in terms of salinity. In contrast, long-term transport potential for POPs by  
100 plastic debris, based on mass fluxes, was suggested to be of less importance compared to  
101 other pathways such as atmospheric transport and transport of dissolved compounds by ocean  
102 currents (Zarfl and Matthies, 2010).

103 Browne et al. (2010) showed that microplastics were abundant in the intertidal zone in the  
104 Tamar estuary (UK) and Costa et al. (2011) showed that plastic debris is also found buried in  
105 estuarine sediments. Salinity, temperature and the presence of dissolved organic matter  
106 appear to be the main parameters governing the solubility of hydrophobic organic compounds  
107 such as POPs (Delle Site, 2001). Therefore, it is important to investigate the effects of each of  
108 these parameters on the sorption and desorption of POPs by microplastics. The assessment of  
109 sorption behaviour of POPs and their transport by microplastics is an important factor in their

110 environmental risk assessment required to reach Good Environmental Status (GES) as part of  
111 the quality descriptor 10 of the Marine Strategy Framework Directive (MSFD 2008/56/EC).  
112 MSFD aims to establish “a framework within which Member States shall take the necessary  
113 measures to achieve or maintain GES in the marine environment by the year 2020”.

114 The present study investigated the sorption behaviour of phenanthrene (Phe) and DDT onto  
115 unplasticised polyvinyl chloride (uPVC) and ultra high molecular weight polyethylene (PE),  
116 due to their widespread presence in the marine environment (Browne et al., 2011; Frias et al.,  
117 2010; Graham and Thompson, 2009; Ng and Obbard, 2006; Thompson et al., 2009), at  
118 different salinities to represent transition zones from riverine to marine waters. A transport  
119 model, taking into account reported environmental concentrations of the two contaminants  
120 for riverine, estuarine and marine waters, is also proposed in order to characterise any  
121 potential risks.

122

## 123 **Materials and methods**

### 124 *Sample preparation and characterisation*

125 Unplasticised polyvinyl chloride (uPVC) and ultra high molecular weight (UHMW)  
126 polyethylene powder (Goodfellow, Huntington, UK) were sieved to the size range 200 – 250  
127 µm to be representative of microplastics found in marine waters (Doyle, 2008; Thompson et  
128 al., 2004). PVC and PE were selected as plastics for study due to their widespread presence in  
129 the marine environment (Frias et al., 2010; Graham and Thompson, 2009; Ng and Obbard,  
130 2006). Seawater was filtered (Whatman membrane filter cellulose nitrate 0.45 µm pore size)  
131 and autoclaved before use to reduce microbial activity and to remove any suspended

132 particulate matter (SPM). The salinity range under investigation was 0, 25, 50, 75 and 100 %  
133 seawater corresponding to 0 (690  $\mu\text{S}/\text{cm}$ ), 8.8, 17.5, 26.3 and 35 psu (practical scale unit).

134

### 135 *Sorption of phenanthrene and DDT to plastics*

136 Analysis of samples over a period of 360 hours showed that equilibrium concentrations in  
137 seawater and on the plastic were reached after 24 hours (Bakir et al., 2014). Equilibrium  
138 sorption time of POPs onto plastics in MilliQ only was also investigated over a period of 360  
139 hours. Details of the selected radiolabeled contaminants, suppliers and concentration range  
140 are listed in Table 1. The concentration range for Phe ( $0.6 - 6.1 \mu\text{g L}^{-1}$ ) was relevant to  
141 environmental concentrations as Phe predominantly enters the marine environment in large  
142 pulses through storm waters (Teuten et al., 2007). The concentration range used for DDT in  
143 seawater ( $0.8 - 3.1 \mu\text{g L}^{-1}$ ) was lower due to lower concentrations of this legacy pollutant that  
144 are typically encountered in the marine environment (Carvalho et al., 2009; Tan et al., 2009).

145 Sorption experiments were conducted in an ISO9001 accredited radioisotope facility at  
146 Plymouth University. Either PVC or PE (10 mg) were placed into each of 12 glass centrifuge  
147 tubes (50 mL) and an increasing concentration of the POP was added to the walls of the tubes  
148 and the solvent allowed to evaporate. 25 mL of seawater were added and the tubes were  
149 capped and equilibrated in the dark for 24 hours at  $18^\circ\text{C}$ , with continuous horizontal, rotary  
150 agitation (220 rpm). All sorption experiments were conducted in triplicate.

151 The concentration of Phe or DDT was determined in the aqueous and solid phases by  
152 counting the  $\beta$  decay from the  $^{14}\text{C}$ -Phe and  $^{14}\text{C}$ -4,4'-DDT by liquid scintillation counting  
153 (LSC) in Ultima Gold (Perkin-Elmer) scintillation cocktail. To measure the aqueous Phe and  
154 DDT concentrations, 5 mL of seawater was added to scintillation cocktail and counted by

155 LSC (Beckman LS 6500 scintillation system). To determine the Phe and DDT concentrations  
156 on the sorbents, plastic particles were collected by filtration (Whatman membrane filter  
157 cellulose nitrate 0.45  $\mu\text{m}$  pore size), added to 5 mL scintillation cocktail and counted directly  
158 by LSC. Data indicated that the presence of  $\leq 10$  mg plastic did not quench the signal or  
159 affect the count rate (Teuten et al., 2007). The amount of contaminant in each phase was  
160 quantified using a calibration curve prepared by counting known amounts of the contaminant.  
161 Total recovery and recovery for each phase are listed in the supplementary information  
162 (Table S1).

163 The distribution coefficient,  $K_d$ , was calculated using the equation:

164

$$165 \quad K_d = [q_e]_{solid} / [C_e]_{aq.} \quad \text{Eq. [1]}$$

166 where  $q_e$  is the amount of contaminant sorbed onto plastic ( $\mu\text{g kg}^{-1}$ ) at equilibrium and  $C_e$  is  
167 the contaminant concentration in the aqueous phase at equilibrium ( $\mu\text{g L}^{-1}$ ).

168

169 For comparison with the linear model ( $K_d$  values), the data were also analysed with the  
170 Freundlich model (Eq.2). Freundlich sorption isotherms have been widely used to model  
171 binding sorption isotherms for sorbed organic contaminants onto polymers (e.g. Teuten et al.,  
172 2007).

173

$$174 \quad \log q_e = \log K_F + 1/n_F \log C_e \quad \text{Eq. [2]}$$

175



176 where  $q_e$  ( $\mu\text{g kg}^{-1}$ ) is the contaminant concentration on the solid phase at equilibrium,  $C_e$  ( $\mu\text{g}$   
177  $\text{L}^{-1}$ ) is the contaminant concentration in the aqueous phase at equilibrium,  $K_F$  ( $\text{L kg}^{-1}$ ) is the  
178 multilayer adsorption capacity and  $1/n_F$  is the Freundlich exponent and an indicator of the site  
179 energy distribution of a sorbent (i.e. sorbent heterogeneity increases as  $n$  decreases).

180

### 181 *Desorption of contaminants from plastic*

182 In order to characterise the effect of salinity on the desorption rates of contaminants from  
183 plastic, Phe was sorbed to plastics as described above, giving final sorbate concentrations of 2  
184  $- 4 \mu\text{g g}^{-1}$ . The filtered solid phase (10 mg) was transferred to a 100 mL amber jar, and 75 mL  
185 seawater (full salinity, 35 psu) or 75 mL of MilliQ (0 % salinity, 690  $\mu\text{S/cm}$ ) were added.  
186 The jars were equilibrated in the dark in a water bath with rotary agitation (220 rpm).  
187 Aliquots (1 mL) were removed at recorded times (0, 3, 6, 12, 24, 45, 75, 130 and 180 min)  
188 and the aqueous concentration of contaminant was determined by LSC. Plastics were allowed  
189 to settle for 1 min before sampling. The concentration of contaminant on the solid phase was  
190 calculated by difference, taking into account both the amount sorbed to the walls and the total  
191 recovery. All kinetic experiments were conducted in triplicate. Pseudo-first order rate  
192 analyses were used to determine the rate constant for initial desorption, where the extent of  
193 resorption was assumed to be negligible (Teuten et al., 2007). The rate constant ( $k$ ) for the  
194 loss of contaminant from the solid phase was determined from the gradient of plots of  
195  $\ln(C_i/C_{i,0})$  vs. time.

196

### 197 **Statistical analysis**

198 Two-way ANOVAs were applied to characterise any significant differences between the  
199 distribution coefficients of both DDT and Phe onto PVC and PE. Student-Newman-Keuls  
200 (SNK) tests were then used to identify any significant terms. A three factor ANOVA was also  
201 applied with salinity, type of plastic and type of pollutant as fixed factors. A multivariate  
202 analysis was also performed to compare differences of sorption capacity for different  
203 salinities for all POP/plastic combinations. Cochran's test was used to ensure that the data  
204 fulfilled the pre-requisites for parametric analysis and the appropriate data were  $\ln(x+1)$   
205 transformed. As an additional precaution step for any type I errors, a more conservative p  
206 value was selected ( $p < 0.01$ ) where heterogeneous variances remained after transformation.  
207 Analysis was conducted as ANOVA is considered robust to such departure from normality  
208 where large data sets are employed (Underwood, 1997). The tests were carried out using  
209 IBM® SPSS® Statistics version 20 and are presented in the supplementary information.

210

## 211 **Results and discussion**

212 We sought to investigate the effects of salinity on the sorption and transport of persistent  
213 organic pollutants (POPs) by plastic microparticles in riverine, estuarine and marine systems.

214 As model combinations, sorption equilibrium time of DDT onto PVC and Phe onto PE were  
215 investigated in seawater (35 psu) and in MilliQ water over a period of 15 days (Fig.1).

216 Sorption equilibrium was reached in 24 hours and salinity was found to have no significant  
217 effect ( $p > 0.01$  and  $p = 0.229$  and  $p = 0.601$ ) on sorption equilibrium time of Phe onto PE  
218 and DDT onto PVC respectively. This indicates that contaminants will reach equilibrium  
219 conditions onto plastics relatively quickly in freshwater, brackish or marine waters.

220 Differences in salinity produced no significant effects on the distribution coefficient values  
221 calculated for Phe sorption onto plastics (Fig.2, Table S3). However, significantly higher  
222 concentrations of DDT were sorbed onto PVC and PE ( $p < 0.01$ , Table S3) in MilliQ water  
223 compared at higher salinities.  $K_d$  values calculated in MilliQ water for DDT sorption onto  
224 plastics were 1.4 and 1.6 times greater for PVC and PE respectively than using seawater (35  
225 psu).  $K_d$  values calculated for DDT sorption onto PVC than PE showed higher variability than  
226 for Phe (Fig.2) and there was a clear trend of decreasing sorption of DDT with increasing  
227 salinity. Larger  $K_d$  values for DDT sorption onto plastics could be explained by differences in  
228 sorption mechanism between DDT and Phe. We previously suggested that DDT sorption onto  
229 polymer follows a partition and pore-filling mechanism as opposed to Phe which may only  
230 occurs through a pore-filling mechanism, thus explaining higher affinity of DDT for plastic  
231 (Bakir et al., 2012; Obst et al., 2011). As aqueous solubility of DDT decreases with an  
232 increase in salinity, salinity might be a greater concern for the sorption of DDT onto plastics  
233 than for Phe. As salinity had no effect on Phe, following a pore-filling mechanism, salinity  
234 may have decreased the partitioning of DDT onto plastics. Solubility of organic compounds  
235 decreases with an increase in salinity and salt content in aqueous phase affects partitioning of  
236 organic chemicals into other phases (Borrirukwisitsak et al., 2012).

237 The Freundlich model fitted the experimental data well with high correlation coefficients  
238 (Fig.S5 and S6 and Table 2). However, differences in salinity had no effects on the sorption  
239 capacity of the two plastics as shown by the Log  $K_F$  values (Fig.S7). This indicates that the  
240 sorption behaviour of these two plastics for the two POPs will be influenced by the  
241 environmental concentrations of the contaminant, independently of salinity. Log  $K_F$  values  
242 were the lowest for Phe sorption onto PVC, followed by Phe sorption onto PE. Highest  
243 values were found for DDT sorption onto PE and PVC. Consequently, PVC and PE have the  
244 potential to sorb and transport relatively higher amounts of DDT than Phe.

245 A study by Karapanagioti et al. (2005), on Phe sorption onto different sorbents, also showed  
246 that salinity did not affect the kinetics of sorptive uptake by PE and polyoxymethylene resins  
247 (as compared to materials containing organic matter), although the sorption equilibrium point  
248 was higher (Karapanagioti et al., 2005). In the present study, salinity did not have any  
249 significant effect on the sorption equilibrium kinetics of DDT onto PVC.

250 Sorption behaviour of POPs onto polymers can be compared to sorption onto sediments  
251 following a dual-mode model comprising a partitioning and adsorption domain due to the  
252 presence of soil organic matter (SOM) (Xing and Pignatello, 1997; Xing et al., 1996; Zhao et  
253 al., 2002). However, the effects of salinity appear to be different for marine sediments  
254 probably due to the presence of organic carbon which showed a positive correlation between  
255 Phe sorption onto sediments and the organic carbon content (Brunk et al., 1996; Yang and  
256 Zheng, 2010). Indeed, the sorption behaviour of phenanthrene on marine sediments, showed  
257 that the initial rate and equilibrium rate constant of adsorption increased with an increase in  
258 salinity (Yang and Zheng, 2010). Another study by Xu et al. (2009) showed that sorption of  
259 benzyl butyl phthalate (BBP) on the sediments also increased with salinity. As the sorption  
260 potential of a POP is regulated by its solubility, an increase in salinity reduces its solubility  
261 and therefore is likely to facilitate its association with sediments (Xu and Li, 2009). This is  
262 supported by an earlier study from the same authors on the adsorption behaviour of dibutyl  
263 phthalate (DBP) which showed that a decrease in salinity decreased the amount of DBP  
264 adsorbed on the sediment (Xu and Li, 2009). Brunk (1997) also suggested that an increase in  
265  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  might cause the dissolved organic matter (DOM) to precipitate and to coat  
266 sediments increasing their organic content and thus their sorption capacity for POPs. The  
267 same can therefore be applied for buried plastic materials being coated by organic matter,  
268 potentially increasing their sorption capacity for pollutants.

269

270 *Desorption kinetics of contaminants from plastic*

271 Salinity was found to have no significant effects on the desorption rates of sorbed Phe and  
272 DDT from PVC and PE (Table 3,  $p > 0.01$ , Table S4). Linear plots are shown in the  
273 supplementary information (Fig. S8 and S9). Desorption rates for DDT from plastics were  
274 much slower than for Phe ( $p < 0.01$ , Table S4) but no significant differences were found  
275 considering the plastic type ( $p = 0.087$ , Table S4).

276

277 *Transport of persistent organic pollutants (POPs) onto plastics from riverine to marine*  
278 *systems*

279 Salinity had little effect, at least for the combinations used herein, on the sorption of  
280 microplastics for POPs. If this is generally true for other plastic/contaminant combinations,  
281 transport of contaminants from riverine to marine waters is likely to be more dependent on  
282 the POP concentration and transport behaviour of microplastics including their residence time  
283 in each system (riverine, estuarine or marine) than the type of plastic. Phe and DDT are found  
284 in higher concentrations in estuaries compared to riverine and marine waters (Tables 2 and  
285 S5). This is not surprising since most anthropogenic organic contaminants (POPs) come from  
286 land sources, with estuaries acting as a “sink”, especially for POPs transported by sediments  
287 (Ridgway and Shimmield, 2002; Zhou et al., 1999).

288 Using the distribution coefficients ( $K_d$ ) values measured herein, the amount of Phe and DDT  
289 sorbed onto PVC and PE was estimated and plotted for the different systems (rivers, estuaries  
290 and marine environment) (Fig.3), using typical aqueous concentrations for these  
291 environments (average values shown in Table 4, full concentration listed in Table S5).

292 Statistical analysis showed significant differences between POP concentrations expected on  
293 plastics for the different POP/plastic combinations ( $p < 0.01$ ). The concentration of POP  
294 sorbed onto plastics followed the order: Phe-PE  $\gg$  DDT-PVC = DDT-PE = Phe-PVC.  
295 Significant differences ( $p < 0.01$ ) were also observed for POP uptake within the different  
296 compartments (riverine, estuarine and marine waters) with some exceptions. Statistical  
297 analysis showed that sorbed concentration of POPs from plastics was higher for estuaries  
298 (salinity 17.5) than for freshwater and marine waters ( $p < 0.01$ , Fig.3).

299 Statistical analysis also showed that the concentrations of POPs in each environment were  
300 more important ( $p > 0.01$  and  $p = 0.718$ ) than the nature of the plastic ( $p < 0.01$  and  $p = 0.001$ ,  
301 Table S4). Therefore the uptake and transport of POPs by plastics in estuarine conditions will  
302 be more related to the input concentrations of the pollutants than the type of polymer present  
303 as a carrier.

304 The amount of contaminants sorbed onto plastics is expected to be greater for plastics in  
305 estuaries as compared to riverine or marine waters because aqueous POP concentrations are  
306 greater in these environments (Fig.3). Sorption equilibrium will be directly dependant on the  
307 transport of microplastics from riverine to marine waters, including particle residence time  
308 for each system. Our results indicate that sorption equilibrium was reached within 24 hours  
309 with no significant effect of salinity. As a result freshwaters, estuaries and marine waters  
310 could be considered as single compartments where particles are continuously exposed to  
311 organic pollutants at different concentrations. Previous studies have shown that sorption  
312 equilibrium for Phe, DDT, perfluorooctanoic acid (PFOA) and di-2-ethylhexyl phthalate  
313 (DEHP) onto PVC and PE is reached within 24-48 hours (Bakir et al., 2014). As a result,  
314 sorption of POPs onto microplastics is expected to reach equilibrium before their release to  
315 the marine environment.

316 As discussed by Ballent et al. (2012) a series of factors will influence the transport of  
317 microplastics from riverine to marine waters. Intrinsic properties of the plastic such as density,  
318 shape and size and external factors such as seawater density, seabed topography, flow  
319 velocity, turbulence and pressure will dictate the particle retention time in each system (rivers,  
320 estuaries and sea). It has also been suggested that transport of microplastics in rivers may be  
321 similar to the transport of sediments (Ballent et al., 2012; Browne et al., 2010; Costa et al.,  
322 2011; Galgani et al., 2000). Fine sediments are carried in suspension (Uncles and Stephens,  
323 2010), which is also suspected to be the main transport mechanism for microplastics. Particle  
324 transit and retention time will therefore be dependent on several factors such as particle size,  
325 and factors specific to the type of estuary such as geographical, meteorological (winds) and  
326 morphological settings, stratification and flushing time. Other factors, such as the presence of  
327 organic matter or the presence of biofilms, have also been suggested, facilitating the retention  
328 of suspended particles in estuaries (Uncles and Stephens, 2010) or by increasing their  
329 sorption capacity for pollutants (Brunk et al., 1996). Browne et al. (2010) suggested that  
330 small particles of sediment and plastic are both likely to settle slowly from the water-column  
331 and are likely to be transported by the flow of water and be deposited in areas where the  
332 water movements are slower.

333 Desorption studies indicated that desorption rates will remain consistent independent of  
334 salinity. Amounts of desorbed contaminants are expected to be greater in estuaries where  
335 particle retention time is expected to be the longest (Ballent et al., 2012). Overall, desorption  
336 rates of Phe from plastics in water were found to be faster than for DDT which is suspected to  
337 remained sorbed onto plastics. The time required for the concentration of the contaminant  
338 onto plastic in estuaries to reach to the concentration of sorbed contaminants in marine waters  
339 was estimated using eq.3 and using desorption rates calculated in this study (Fig.S10 and  
340 Table S6).

341

342  $C = C_0 \exp(-kt)$  Eq. [3]

343

344 where  $C_0$  is the initial POP concentration onto plastic ( $\mu\text{g g}^{-1}$ )  $C$  is the concentration of the  
345 POP onto plastic ( $\mu\text{g g}^{-1}$ ) at time  $t$  (in days) and  $k$  is the desorption rate constant for the first  
346 order model ( $\text{day}^{-1}$ ).

347

348 The results indicated that 5 days were required for the concentration of Phe sorbed onto PVC  
349 and PE in estuaries to desorb and reach concentration estimated in marine waters (Fig.4). A  
350 much longer timescale was required for DDT desorption from plastics with 13 and 15 days  
351 for PVC and PE respectively. The potential for microplastics to transport pollutants from  
352 estuaries will therefore be dependent on the estuary's cycle including flushing and particle  
353 residence time. Jay et al. (1997) characterised the particle residence time for some estuaries  
354 for different locations. Timescales varied from 3 to 9 months for Chesapeake Bay to 0.5 day  
355 for Plum Island Sound (Jay et al., 1997). For estuaries presenting a short particle retention  
356 time, microplastics are therefore likely to act as vectors for transport of Phe and DDT to  
357 marine waters but with limited exposure to organisms. For estuaries with longer retention  
358 time, such as Chesapeake Bay, desorption of POPs from plastics could be of concern as well  
359 as the exposure of contaminated particles to aquatic organisms. It is however unknown  
360 whether the contaminants sorbed onto plastics can then desorb upon ingestion by marine  
361 organisms at concentrations which may cause significant harm or ecologically adverse effects.  
362 Microplastic ingestion has been documented for a wide range of organisms at many trophic  
363 levels (Avery-Gomm et al., 2012; Besseling et al., 2012; Blight and Burger, 1997; Boerger et



364 al., 2010; Bravo Rebolledo et al.; Browne et al., 2008; Day, 1980; Denuncio et al., 2011;  
365 Lusher et al., 2013) with some evidence of trophic transfer of plastics (Farrell and Nelson,  
366 2013). Transfer of sorbed contaminants from plastic following ingestion has also been  
367 suggested (Tanaka et al., 2013). As estuaries are the most productive ecosystems in the  
368 marine environment and due to the relatively long particle retention time in such systems; it  
369 is highly likely that a wide range of marine organisms are exposed to contaminated  
370 microplastics, but the chemical effects, if any, of this are unknown. Microplastics can enter  
371 the marine environment through land-based sources and are exposed to POPs from  
372 anthropogenic sources, where sorption takes place. Contaminated particles are then  
373 transported into estuaries where they can reside for a relatively long time, depending on the  
374 type of estuary. Contaminated particles can also settle, accumulate or being buried onto  
375 sediments as well as being deposited on the shoreline (Browne et al., 2011; Browne et al.,  
376 2010). Man-made operations involving the suspension of sediments, such as dredging, could  
377 cause a large release of contaminated particles into the marine environment.

378 Estuaries can also been defined as sink of contaminated particles with their pulse release in  
379 marine waters following flushing. Contaminated plastics can also increase in density  
380 following biofouling and as a result can be found at the sea surface microlayer (SML), in the  
381 water column or deposited onto sediments where they are potentially exposed to a wide range  
382 of marine organisms for ingestion.

383

## 384 **Conclusions**

385 Increases in salinity had no significant effects on the sorption capacity of PVC and PE for  
386 Phe; however sorption capacity for DDT was significantly higher in the absence of salinity  
387 suggesting a differential mechanism of sorption for contaminants. The transport capacity of

388 these plastics for DDT and Phe in estuaries will likely be more related to the aqueous  
389 concentration of the contaminants than to the salinity. The transport model proposed showed  
390 that the amount of POPs sorbed by plastics in freshwater, to brackish and marine waters  
391 followed the order: Phe-PE >> DDT-PVC = DDT-PE >> Phe-PVC. Microplastics have the  
392 potential to sorb substantially more contaminants in estuaries due to higher reported  
393 concentrations of contaminants than in riverine and marine waters. Sorption equilibrium of  
394 POPs onto microplastics is also expected to be reached in each system due to their long  
395 particle residence and potential storage in estuarine sediments. As desorption rates of sorbed  
396 contaminants were not affected by salinity, amounts desorbed are expected to be correlated to  
397 the particle retention time in estuaries and marine waters. The proposed transport model  
398 suggested that estuaries can represent an important source for contaminated microplastics  
399 with their pulse release to the marine environment through natural (e.g. flushing) and  
400 anthropogenic processes (e.g. dredging).

401 This study suggests that the risk assessment for the potential for microplastics to cause harm  
402 in the environment, as part of the MSFD, should not be limited to the marine environment but  
403 also include estuarine systems which are suspected to represent an important source and sink  
404 of contaminated plastics.

405

#### 406 **Acknowledgements**

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408 (DEFRA) in the United Kingdom as part of a larger project investigating the potential for  
409 microplastics to cause harm in the marine environment (Grant number ME5416).

410

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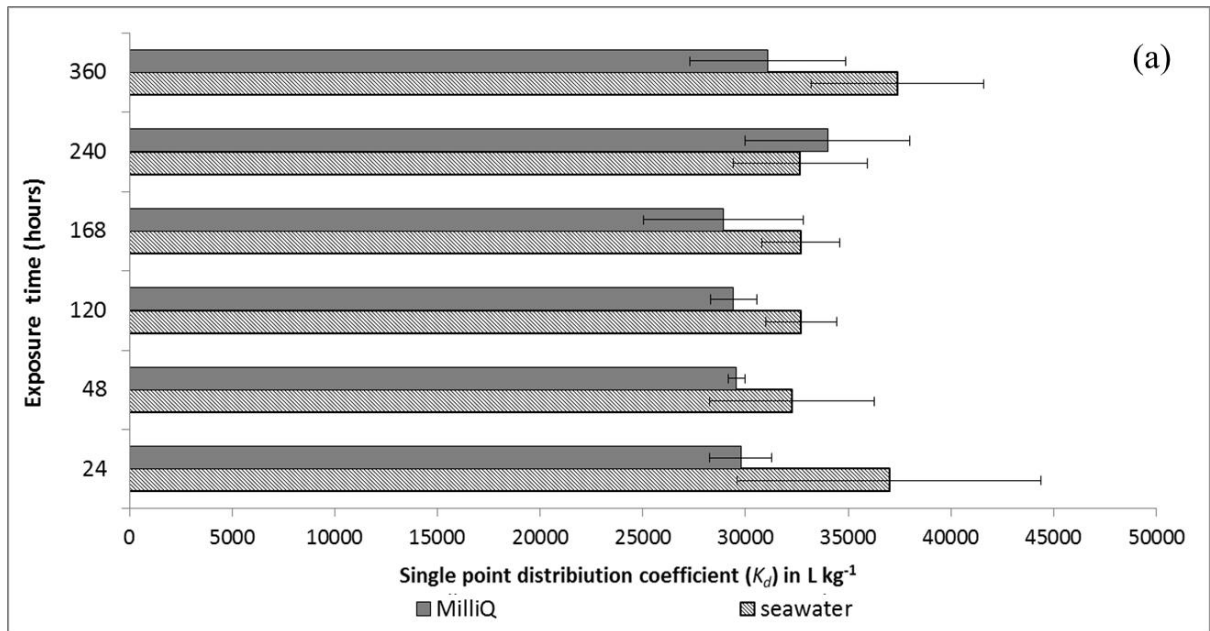
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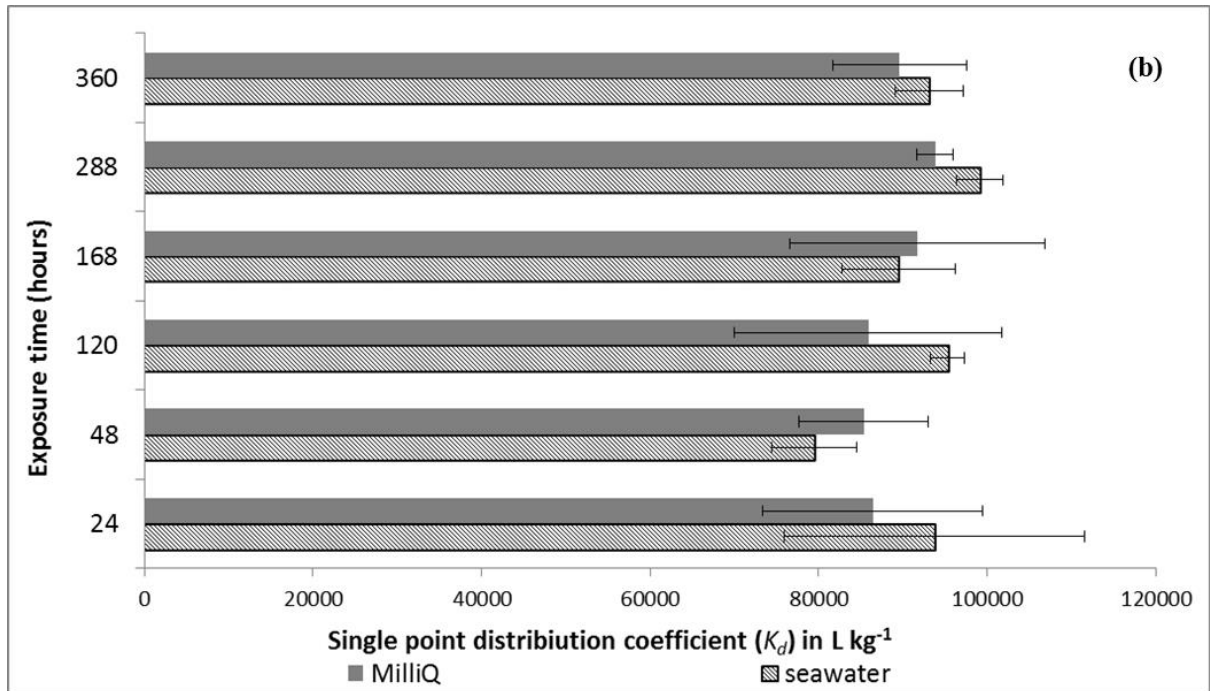
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### Figures



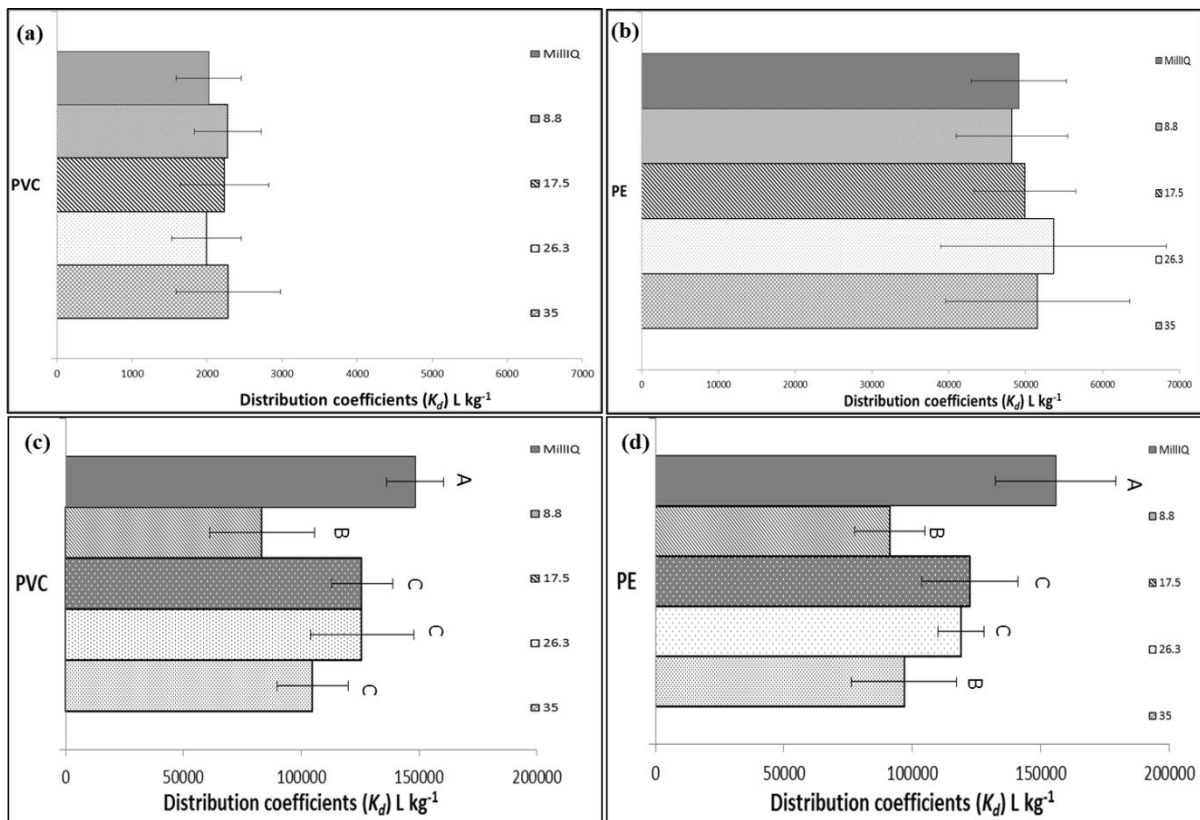
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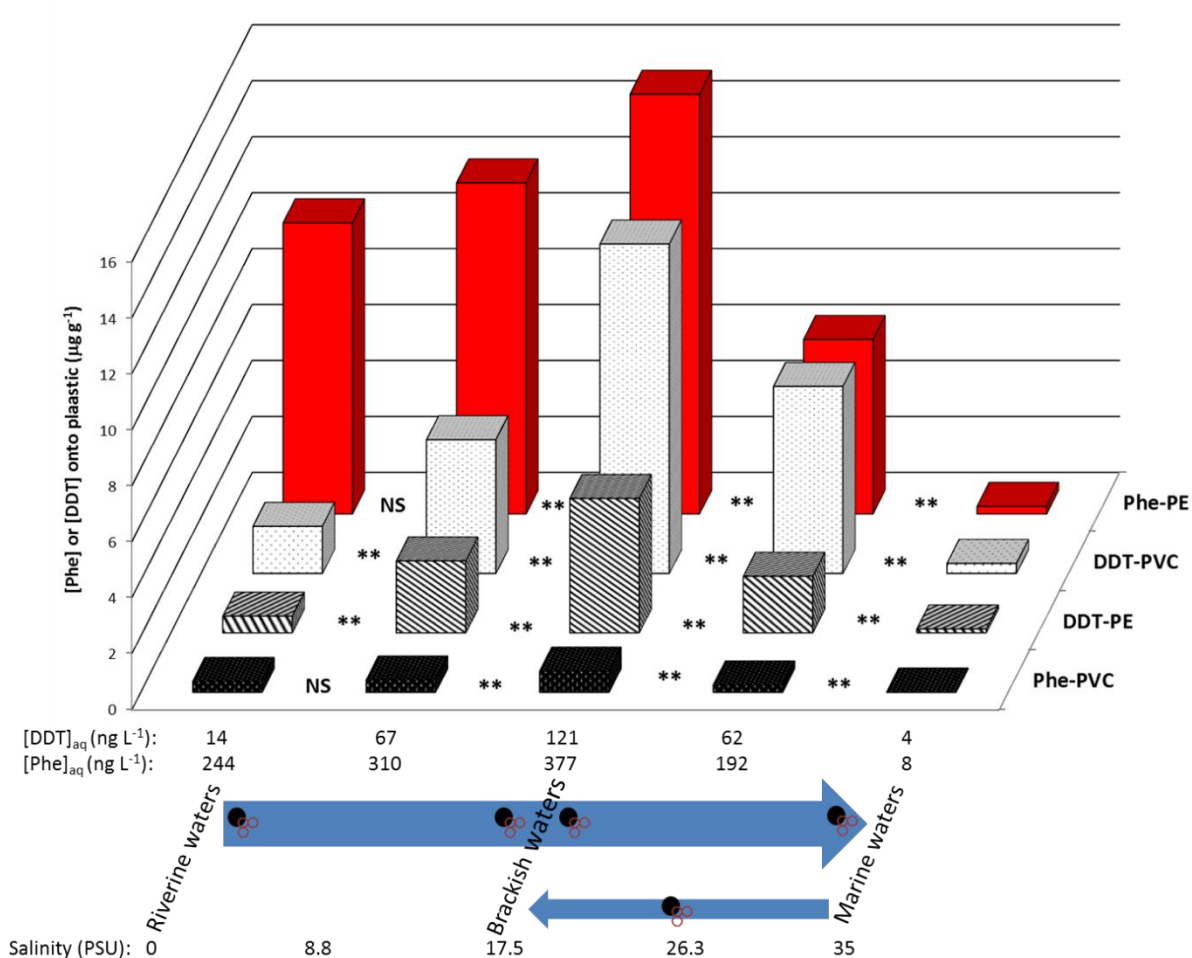
574 Fig.1 Sorption equilibrium time of (a) Phe onto PE and (b) DDT sorption onto PVC in  
575 seawater (35 psu) and in MilliQ water (n = 3, ± SD).

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Fig.2 Distribution coefficients ( $K_d$ ) calculated from the sorption of Phe onto (a) PVC, Phe onto (b) PE, DDT onto (c) PVC and DDT onto (d) PE for different salinities ( $n = 3, \pm$  SD). (A, B, C: no significant differences between  $K_d$  values;  $p < 0.01$ ).



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586 Fig.3 Potential for microplastics to sorb and transport phenanthrene (Phe) and DDT in  
 587 riverine, estuarine and marine waters according to reported typical environmental  
 588 concentrations of Phe and DDT. Calculated amounts sorbed onto plastics via  $K_d$   
 589 values measured herein. Statistics analysis carried-out between sorbed amounts of  
 590 contaminants for each POP/plastic combination for the different ecosystems: \*\*  $p <$   
 591 0.01; ns: not significant

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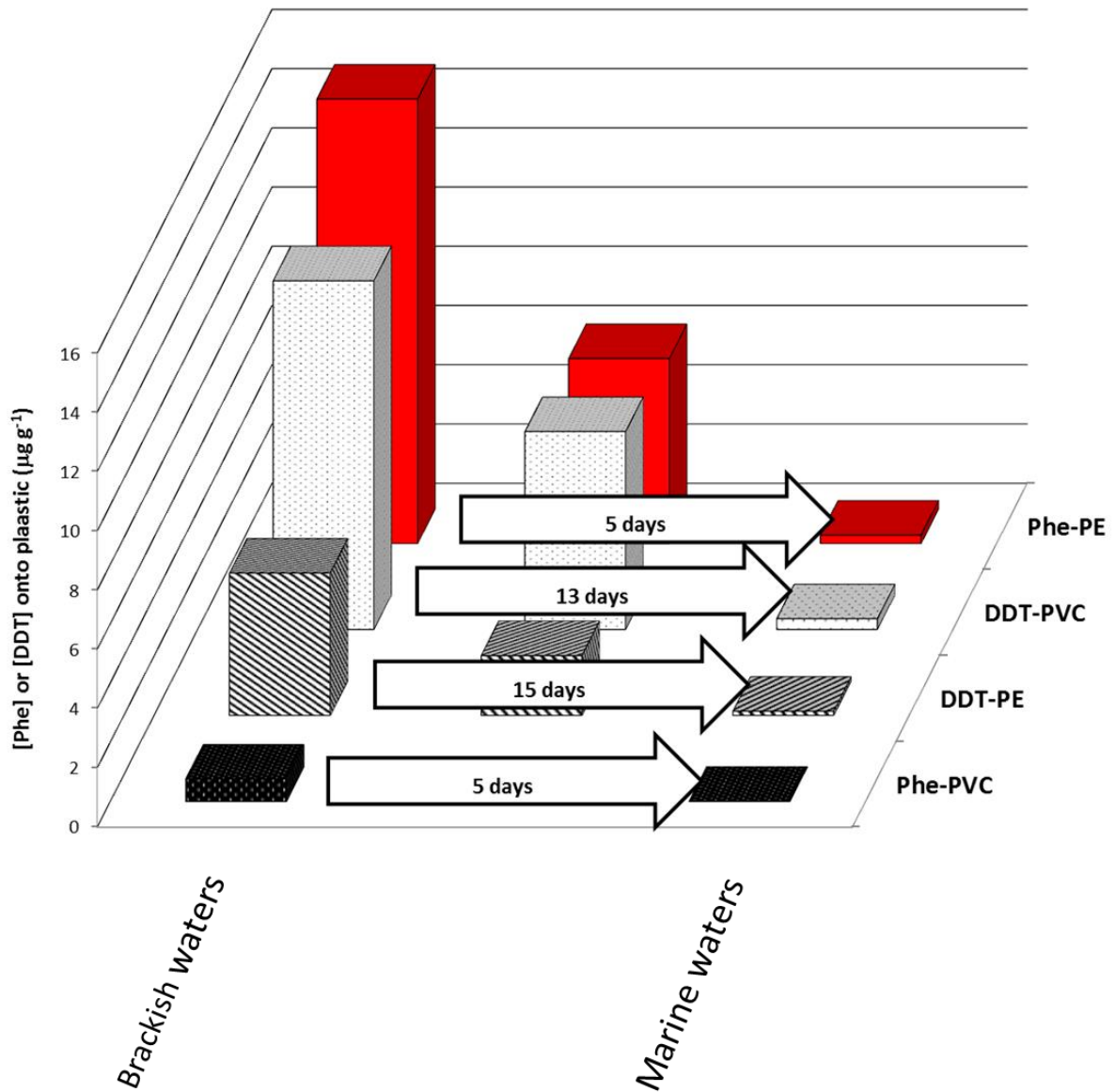
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598 Fig. 4 Time required (in days) for contaminants sorbed onto plastics in estuaries to reach

599 concentration of estimated sorbed contaminants onto plastics in marine waters.

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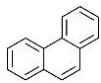
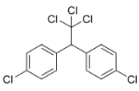
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## Tables

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608 Table 1. Pollutants under investigation and associated parameters.

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Pollutant	Chemical structure	Initial concentration ( $\mu\text{g L}^{-1}$ )	Specific activity (MBq/mmol)	Supplier	Solvent	MW ( $\text{g mol}^{-1}$ )	Distilled water	Log Kow
$^{14}\text{C}$ -Phe		0.6-6.1	303.4	Sigma - Aldrich	Methanol	178.23	600 (22°C) (EPA, 2013)	4.5 (MacKay et al. (1993))
$^{14}\text{C}$ -DDT		0.8-3.1	370-110	ARC, Inc.	Ethanol	354.49	25 (25°C) (Registry, 2013)	6.36 (Walker (2008))

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618 Table 2. Freundlich parameters from the sorption of phenanthrene (Phe) and DDT onto PVC  
 619 and PE for different salinities

		Salinity range (PSU)				
		0 (MilliQ)	8.8	17.5	26.3	35
<b>PVC-Phe</b>	Log $K_F$ (L kg <sup>-1</sup> )	3.3	3.4	3.3	3.3	3.3
	$n_F$	0.88	1.01	0.84	0.84	0.87
	R <sup>2</sup>	0.975	0.966	0.954	0.969	0.95
<b>PE-Phe</b>	Log $K_F$ (L kg <sup>-1</sup> )	4.7	4.8	4.9	5.1	4.9
	$n_F$	0.94	0.89	0.86	0.72	0.84
	R <sup>2</sup>	0.995	0.986	0.995	0.979	0.96
<b>PVC- DDT</b>	Log $K_F$ (L kg <sup>-1</sup> )	5.8	5.9	5.5	5.3	5.4
	$n_F$	0.70	0.63	0.71	0.87	0.82
	R <sup>2</sup>	0.99	0.991	0.988	0.979	0.988
<b>PE-DDT</b>	Log $K_F$ (L kg <sup>-1</sup> )	5.6	5.6	5.6	5.3	5.9
	$n_F$	0.79	0.71	0.72	0.87	0.60
	R <sup>2</sup>	0.973	0.966	0.936	0.993	0.994

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622

623 Table 3. First order rate constants for desorption of phenanthrene (Phe) and DDT from PVC  
 624 and PE in seawater (full salinity, 39.7) and in MilliQ (n=3,  $\pm$ SE).

Plastic	pollutant	Aqueous solution (salinity, PSU)	Desorption rate (k, day <sup>-1</sup> $\pm$ SD)
PVC	Phe	MilliQ (0)	0.73 $\pm$ 0.26
		Seawater (35)	0.88 $\pm$ 0.56
PE		MilliQ (0)	1.15 $\pm$ 0.12
		Seawater (35)	1.37 $\pm$ 0.45
PVC	DDT	MilliQ (0)	0.21 $\pm$ 0.01
		Seawater (35)	0.26 $\pm$ 0.06
PE		MilliQ (0)	0.20 $\pm$ 0.04
		Seawater (35)	0.23 $\pm$ 0.08

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638 Table 4. Averaged reported environmental concentrations of phenanthrene (Phe) and DDT  
639 for riverine, estuarine and marine waters. Full values are shown in Table S5.

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Ecosystems	Contaminant concentration (ng L <sup>-1</sup> )	
	Phe	DDT
<b>Rivers</b>	243.68	13.97
<b>Estuaries</b>	<b>377.25</b>	<b>120.78</b>
<b>Marine waters</b>	7.5	3.83

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658 **Transport of persistent organic pollutants by microplastics in estuarine**  
659 **conditions**

660

661 **Supplementary information**

662

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669 ***Recovery of contaminants***

670 Table S1. Total recovery (%) of the contaminants (radioactivity) and recovery in each phase

671 (A: aqueous phase, G: glass walls, S: solid phase, T: total) (averaged values, n=12)

672

	Salinity (%)																			
	0				25				50				75				100			
	A	G	S	T	A	G	S	T	A	G	S	T	A	G	S	T	A	G	S	T
DDT-PVC	2	3	76	<b>81</b>	2	3	86	<b>91</b>	2	3	72	<b>77</b>	3	2	82	<b>87</b>	2	1	80	<b>83</b>
DDT-PE	2	3	84	<b>89</b>	2	3	86	<b>91</b>	2	3	72	<b>77</b>	3	2	82	<b>87</b>	2	1	83	<b>86</b>
Phe-PVC	51	2	43	<b>96</b>	51	2	45	<b>98</b>	53	2	48	<b>103</b>	54	2	43	<b>99</b>	46	1	40	<b>87</b>
Phe-PE	4	3	77	<b>84</b>	4	6	72	<b>82</b>	46	1	38	<b>85</b>	4	6	73	<b>83</b>	3	8	81	<b>92</b>

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676 *Sorption equilibrium time*

677 Statistical analysis

678 Table S2. Two factor ANOVA and SNK post-hoc test for the effect of salinity on the sorption  
 679 equilibrium time of (A) Phe onto PE and (B) DDT onto PVC (n=3, ±SD).

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(A)

Source	DF	MS	F	P
exposure time (days)	5	0.033	2.85	0.037
salinity	1	0.003	0.28	0.601
exposure time x salinity	5	0.012	1.07	0.401
SNK tests				
exposure time (days)	1 = 2 = 5 = 7 = 10 = 15			
salinity	MilliQ = seawater			

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(B)

Source	DF	MS	F	P
exposure time (days)	5	0.1808	9.61	< 0.01
salinity	1	0.0287	1.52	0.229
exposure time x salinity	5	0.0045	0.24	0.941
SNK tests				
exposure time (days)	2 < 1 = 5 = 7 = 12 = 15			
salinity	MilliQ = seawater			

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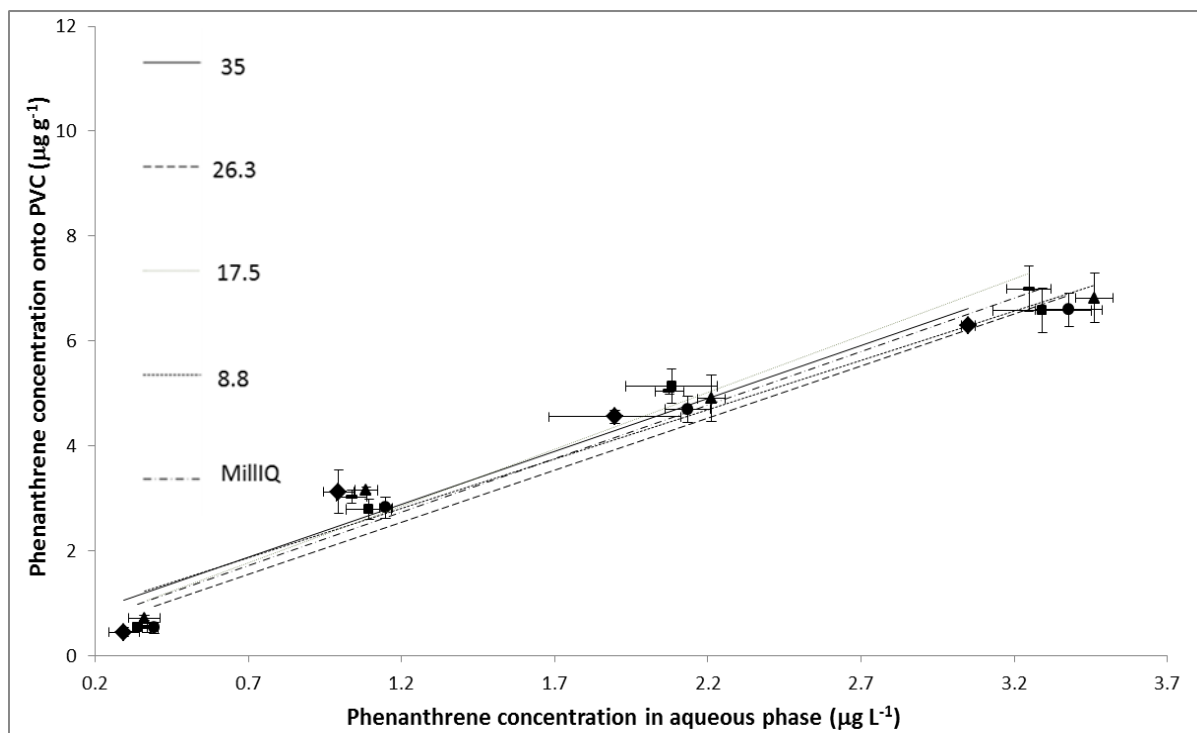
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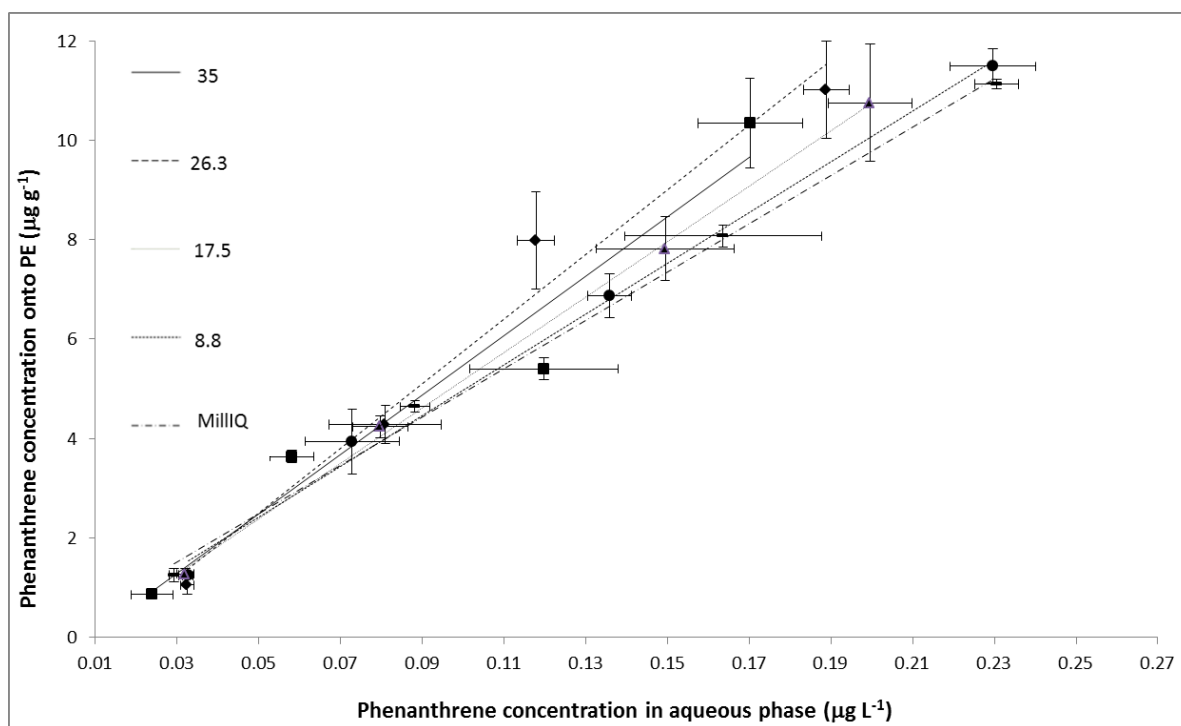
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701 *Binding sorption isotherms*



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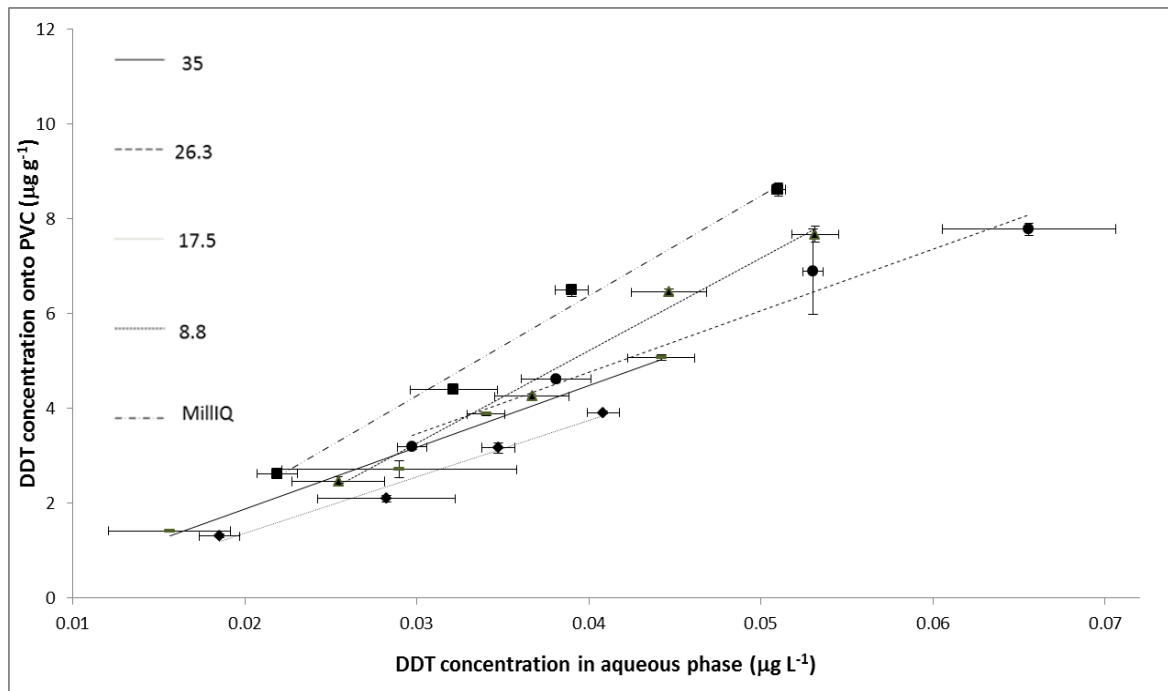
703 Fig.S1 Sorption isotherms of phenanthrene (Phe) sorption onto PVC for different salinities ( $n$   
704  $= 3, \pm \text{SD}$ ).



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706 Fig.S2 Sorption isotherms of phenanthrene (Phe) sorption onto PE for different salinities ( $n$   
707  $= 3, \pm \text{SD}$ ).

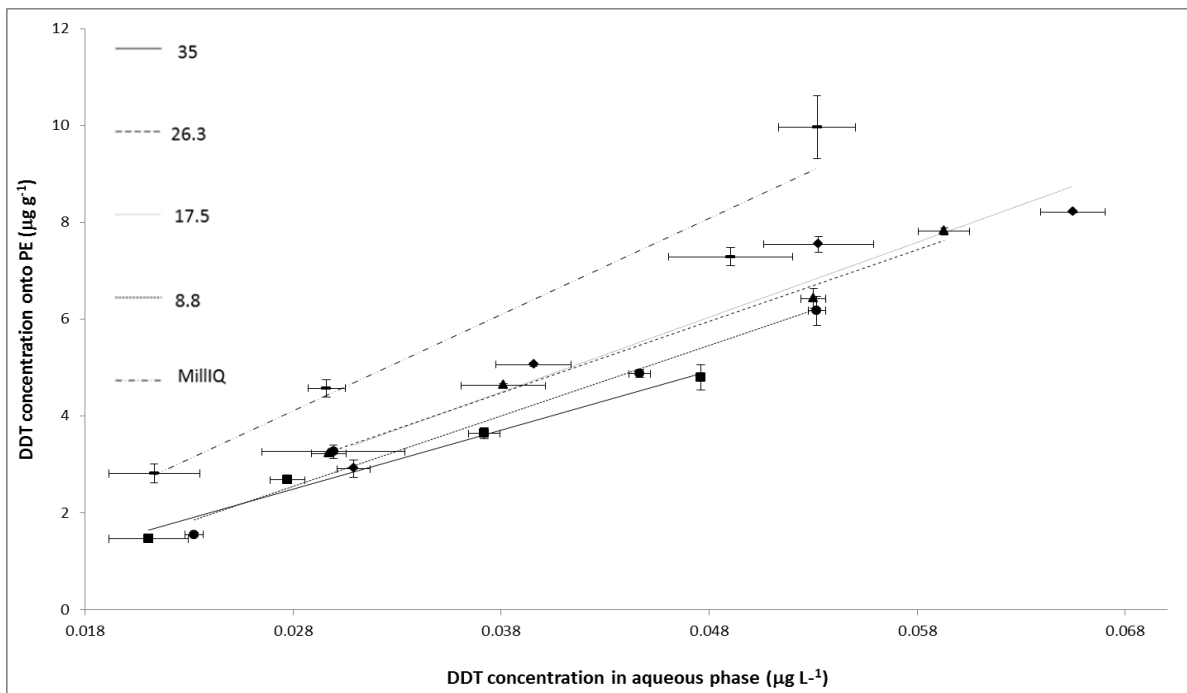




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709 Fig.S3 Sorption isotherms of DDT sorption onto PVC for different salinities (n = 3, ± SD).

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712 Fig.S4 Sorption isotherms of DDT sorption onto PE for different salinities (n = 3, ± SD).

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715 *Statistical analysis*

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717 Table S3. Multivariate analysis and SNK post-hoc test for the effect of salinity on the  
718 distribution coefficient values of POPs onto plastics

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Source	Dependent Variable	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	PVC_Phe	703387.108 <sup>a</sup>	4	175846.777	.616	.653
	PE_Phe	250843050 <sup>b</sup>	4	62710762.46	.652	.628
	PVC_DDT	2.812E+10 <sup>c</sup>	4	7030464098	23.295	.000
	PE_DDT	3.136E+10 <sup>d</sup>	4	7839462287	24.730	.000
Intercept	PVC_Phe	287309124.2	1	287309124.2	1005.975	.000
	PE_Phe	1.519E+11	1	1.519E+11	1580.915	.000
	PVC_DDT	8.124E+11	1	8.124E+11	2691.892	.000
	PE_DDT	8.233E+11	1	8.233E+11	2597.178	.000
salinity	PVC_Phe	703387.108	4	175846.777	.616	.653
	PE_Phe	250843049.8	4	62710762.46	.652	.628
	PVC_DDT	28121856394	4	7030464098	23.295	.000
	PE_DDT	31357849149	4	7839462287	24.730	.000

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**PVC\_DDT**

Student-Newman-Keuls<sup>a,b,c</sup>

salinity	N	Subset		
		1	2	3
8.8	12	83370.2543		
35	12		104784.8951	
26.3	12		119572.9624	
17.5	12		125747.7697	
MilliQ	12			148340.1245
Sig.		1.000	.013	1.000

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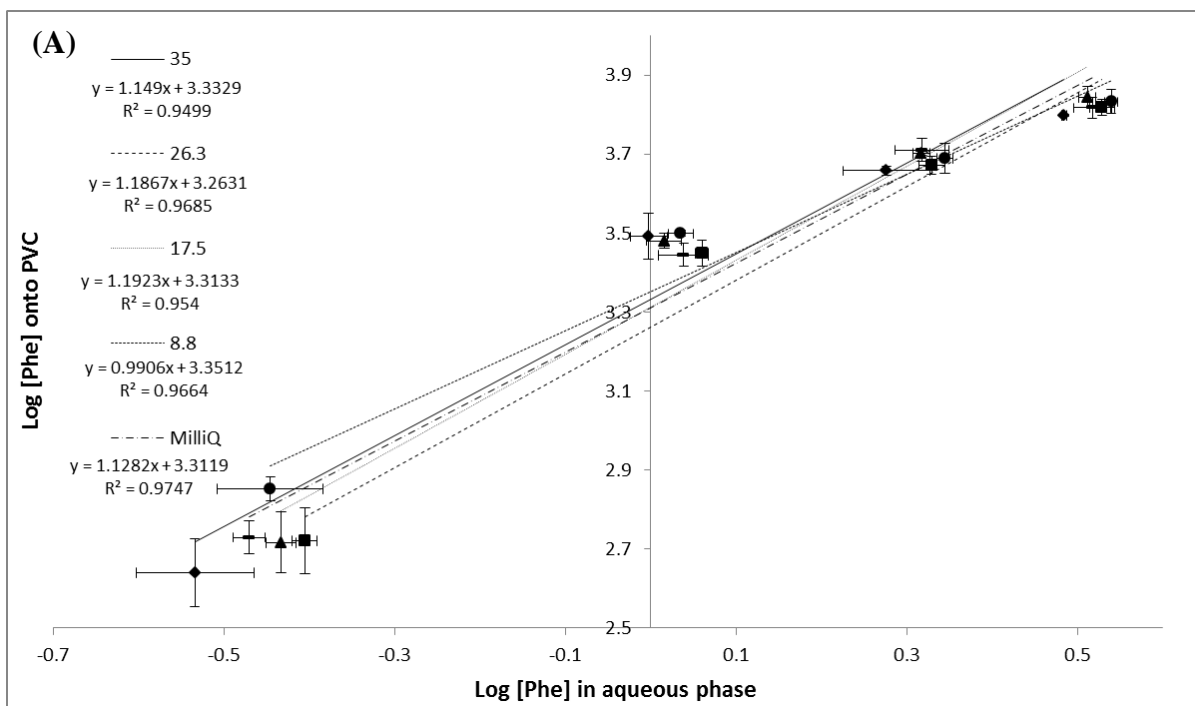
**PE\_DDT**

Student-Newman-Keuls<sup>a,b,c</sup>

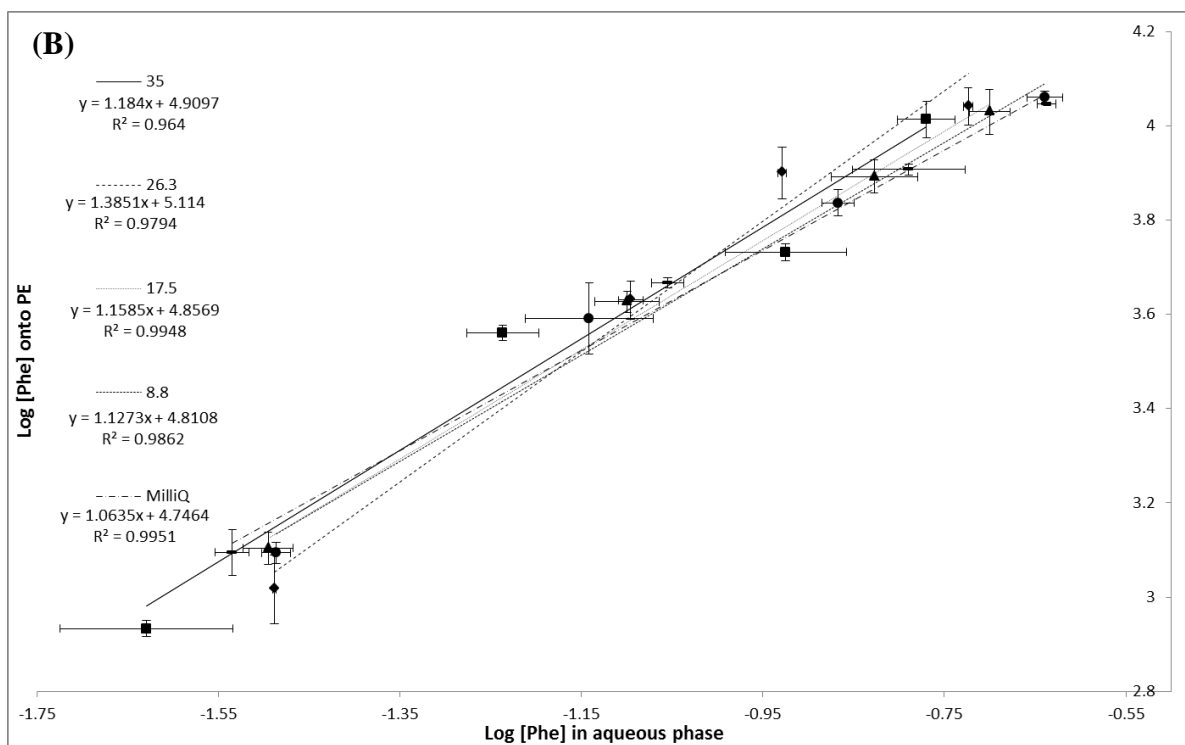
salinity	N	Subset		
		1	2	3
8.8	12	91380.3634		
35	12		96892.4584	
26.3	12		119059.9927	
17.5	12		122393.4584	
MilliQ	12			155977.4443
Sig.		.451	.648	1.000

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726 *Freundlich binding sorption isotherms*



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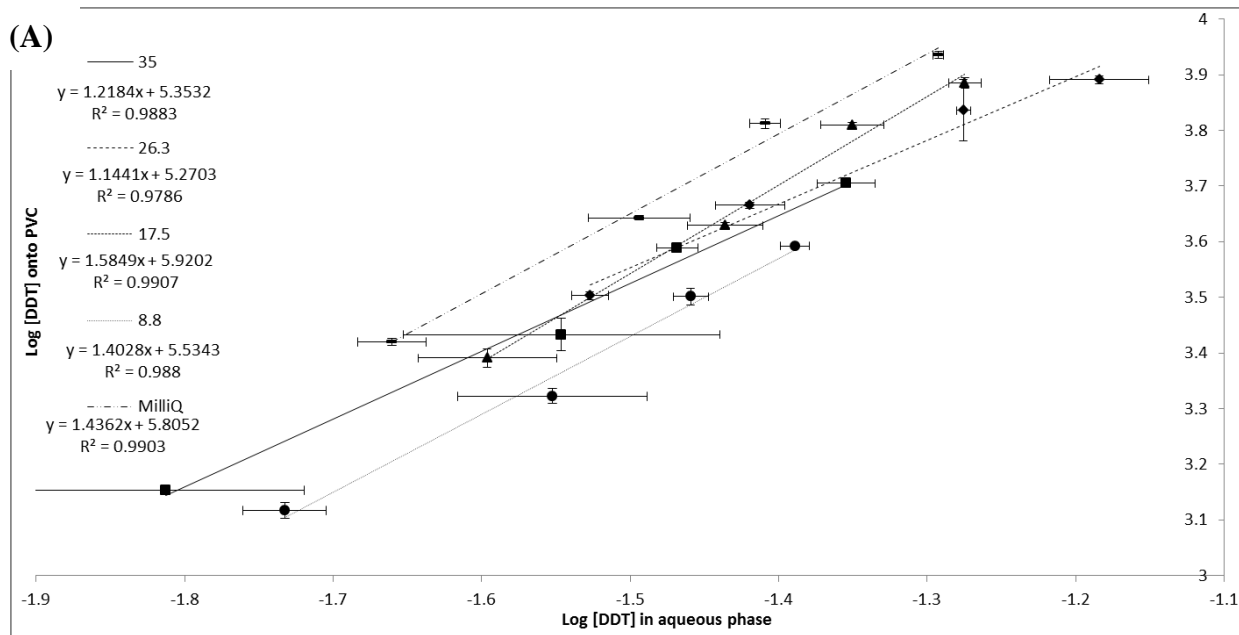


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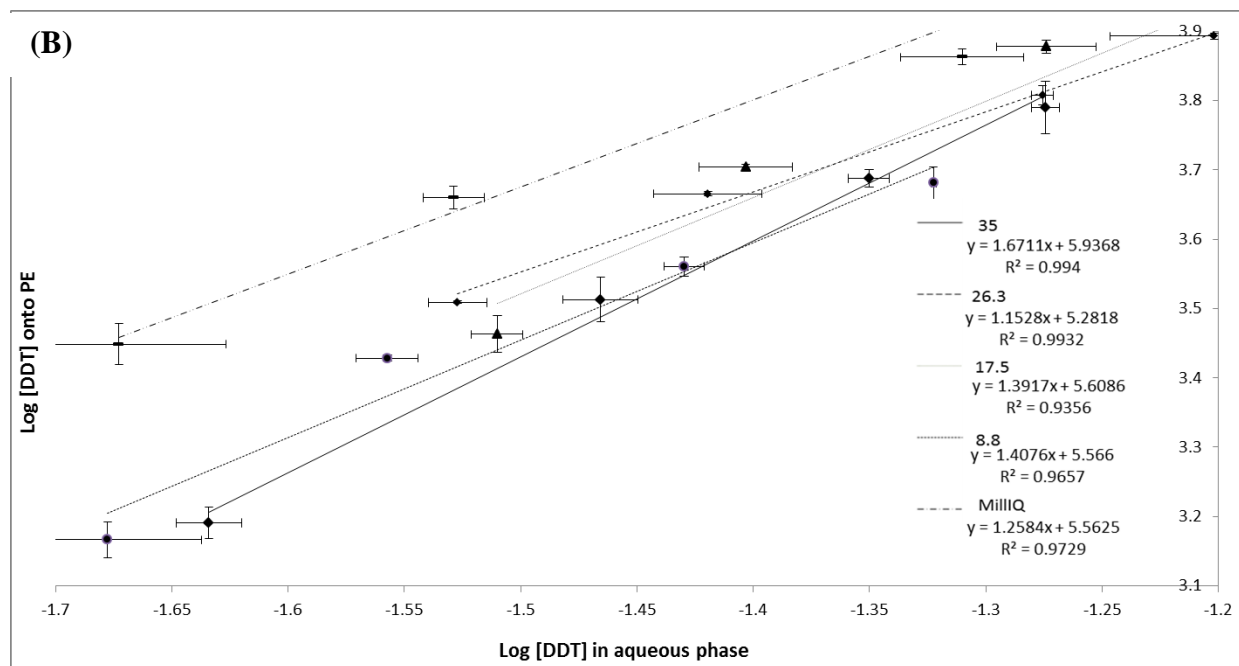
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730 Fig.S5 Freundlich binding sorption isotherms for phenanthrene (Phe) sorption onto (A) PVC  
 731 and (B) PE (n = 3, ± SD).

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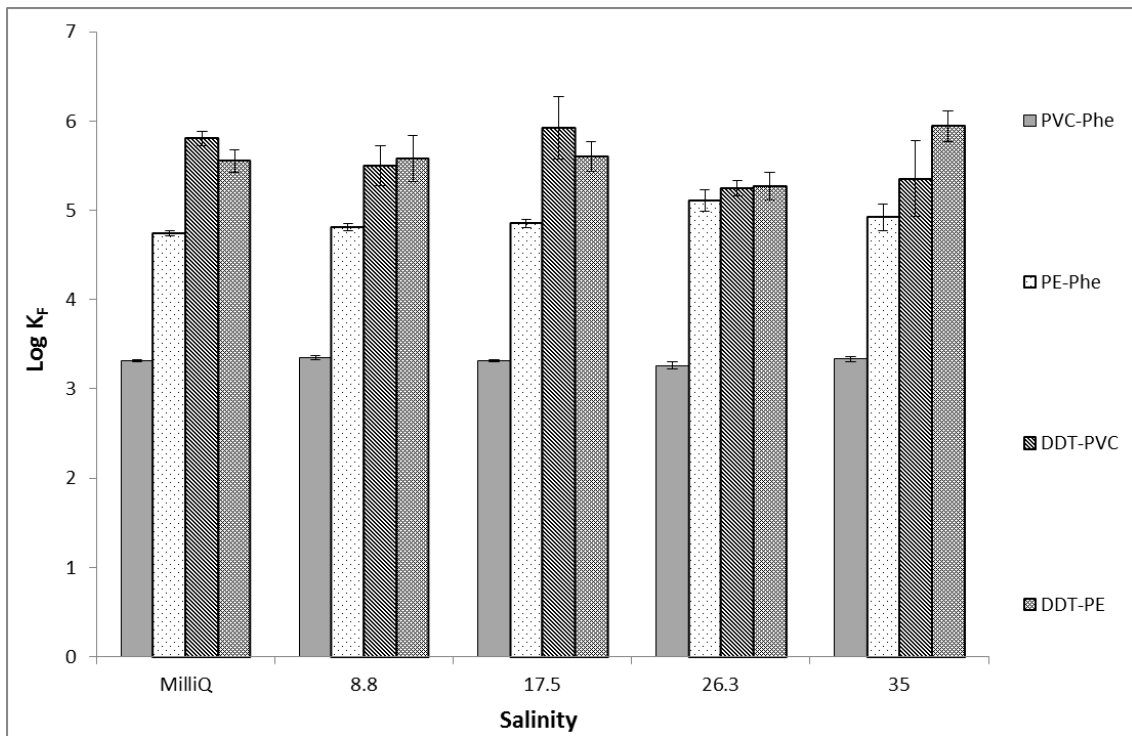
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735 Fig.S6 Freundlich binding sorption isotherms for DDT sorption onto (A) PVC and (B) PE (n  
736 = 3,  $\pm$  SD).

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740 Fig. S7 Log K<sub>F</sub> values as a function of salinity for Phe and DDT sorption onto PVC and PE

741 (n = 3, ± SD)

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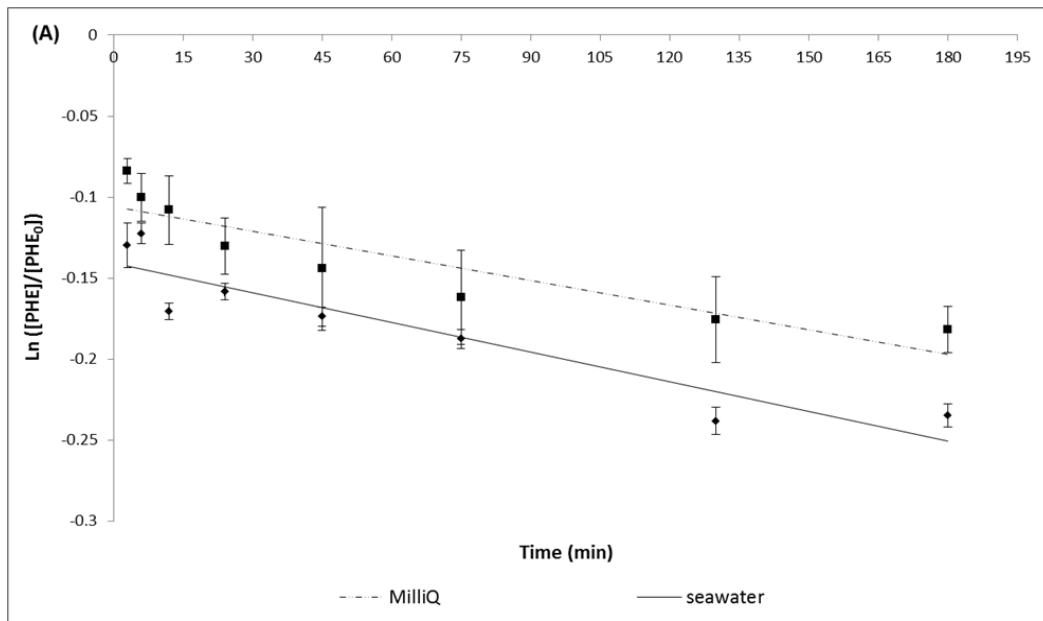
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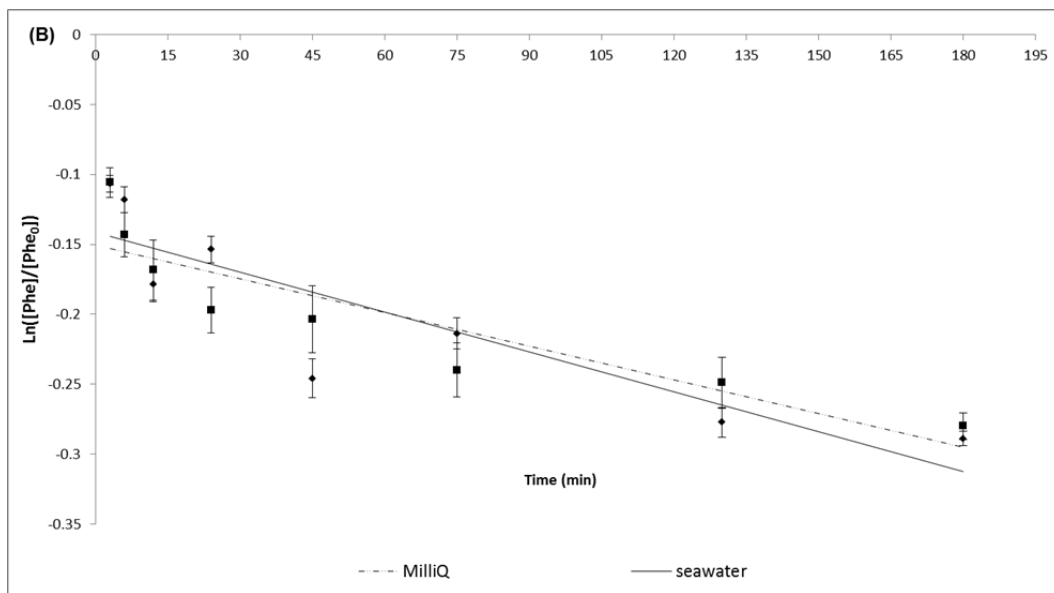
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751 *Desorption of contaminants from plastic*

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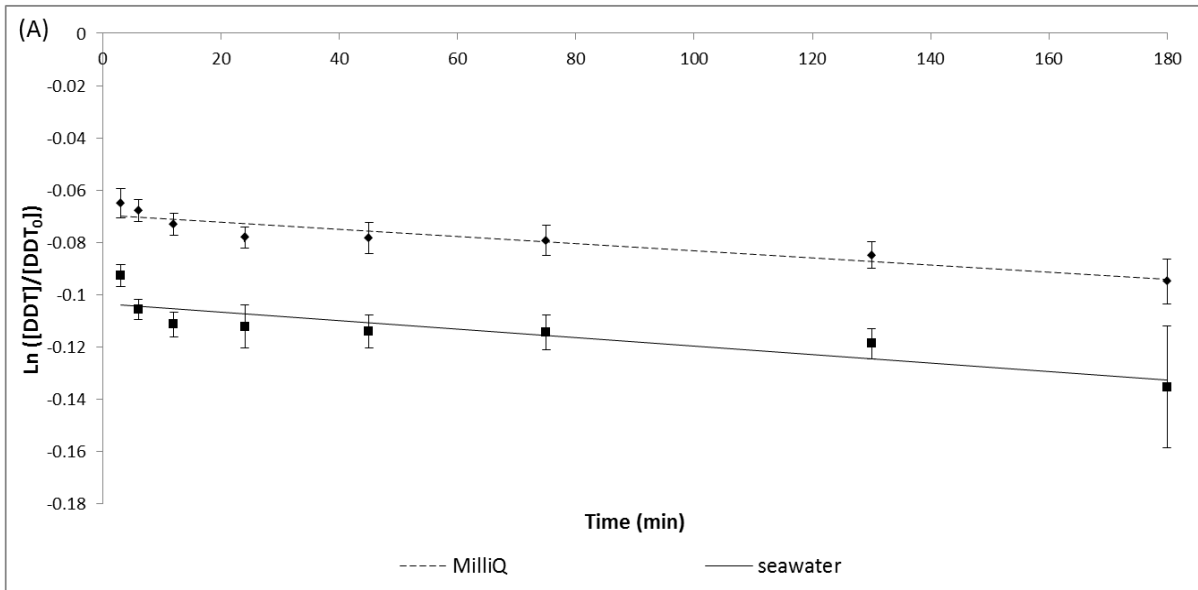


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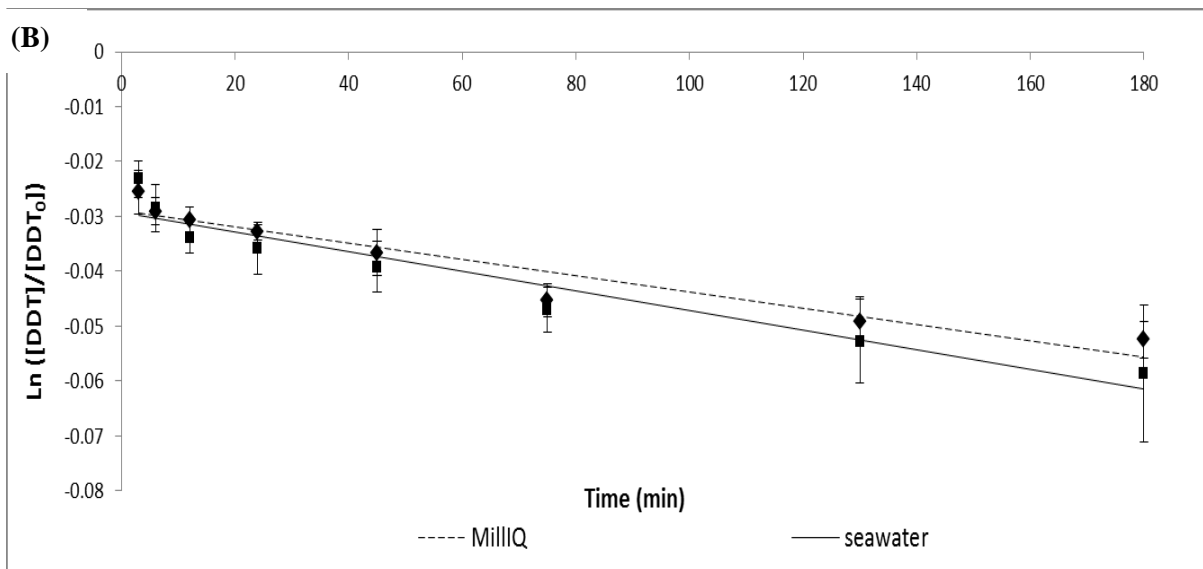
755 Fig.S8 Desorption kinetics of phenanthrene (Phe) from (A) PVC and (B) PE in in MilliQ and

756 in seawater (35 psu) (n = 3, ± SD).

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760 Fig.S9 Desorption kinetics of DDT from (A) PVC and (B) PE in MilliQ and in seawater (35  
 761 psu) (n = 3, ± SD).

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766 *Statistical analysis*

767 Table S4. Three factor ANOVA and SNK post hoc test for the comparison of the effects of  
 768 salinity on the desorption rates of Phe and DDT from PVC and PE.

769

Source	DF	MS	F	P
POP	1	1.434	66.59	< 0.01
plastic	1	0.071	3.32	0.087
salinity	1	0.015	0.71	0.411
POP x plastic	1	0.097	4.49	0.050
POP x salinity	1	0.003	0.13	0.724
plastic x salinity	1	0.0001	0	0.950
POP x plastic x salinity	1	0.0004	0.02	0.899
SNK tests				
POP	Phe >* DDT			
Plastic	PE = PVC			
Salinity	MilliQ = seawater			
POP x plastic	Phe-PVC = Phe-PE >* DDT-PE = DDT-PVC			

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780 *Environmental significance*

781 *Transport of POPs in estuaries*

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783 Table S5. Reported environmental concentrations of Phe and DDT for riverine, estuarine and  
784 marine waters.

785

	Location	Sampling time	Phe	$\Sigma$ DDT	References
<b>River</b>	St. Lawrence River, Canada	1990	n.a.	1.02	Pham et al., 1993
	Henan Reach of the Yellow River, Middle China	2005 - 2006	15.9 – 698.8	n.a.	Sun et al., 2009
	Gao-Ping River, Taiwan	1999 - 2000	< 20 - 240	n.a.	Doong & Lin, 2004
	Pearl River Delta, China	2005 - 2006	n.a.	3.89	Guan et al., 2009
	Yangtze River	1999		1.37	Sun et al., 2002
	Liaohhe River	1998		2.77	Zhang and Dong, 2002
	Huaihe River			4.45 - 78.9	Yu et al., 2004
	Qiantang River	2005		4.9	Zhou et al., 2006
	Jiulong River	2000		12.8	Zhang et al., 2001
	Red River	1998 - 1999		54.2	Hung and Thiemann, 2002
	Ebro River	1998		3.1	Fernández et al., 1999
<b>Estuaries</b>	Dalio River Estuary, China	2007	n.a.	1.7	Tan et al., 2009
	Hailing Bay, South China	2007	n.a.	0.42	Xing et al., 2009
	Minjiang River Estuary	1999	1700	142	Zhang et al., 2003 and 2004
	River Thames	1993-1995	< 3 - 304	n.a.	Law et al., 1997
	River Humber		< 8 - 296		
	River Severn		< 3 - 17		
	River Tamar				
	River Tees		< 8 - 1170		
River Tyne	< 10 - 90				
River Mersey	11 - 73				

	Cadiz Bay	n.s.	266-377	n.a.	Pérez-Carrera et al., 2007
<b>Marine</b>	Gulf of Mexico	2000	n.a.	73-605	Carvalho et al., 2009
	Celtic sea	1993 - 1995	< 6	n.a.	Law et al., 1997
	Irish sea		< 8		
	Offshore Moray Firth		< 8		
	Offshore Liverpool Bay		< 8		
	Smith's Knoll		< 8		
	Bering and Chukchi Sea	1999	n.a.	0.013 – 0.123	Zi-wei et al., 2002
	Bering sea	1978	n.a.	0.02	Kawano et al., 1988
	South China Sea	1989 -1990	n.a.	0.004 – 0.012	Iwata et al., 1993
	Strait of Malacca, Malaysia			0.007	
	Java Sea, Indonesia			0.006	
	Phillipines	1999	n.a.	7.4	UNEP, 2002
	Thailand	1999	n.a.	3.72	
	Viet Nam	1999	n.a.	49.27	
	Singapore	2002	n.a.	0.03 – 2.58	Basheer et al., 2003
	Singapore	2004	n.a.	0.01 – 0.63	Wurl and Obbard, 2005
	Antarctic seas	1981-1982	n.a.	0.02 – 0.24	Tanabe et al., 1983
	Mediterranean	1977 - 1980	n.a.	1	Orlova et al., 1983
	Subarctic Atlantic		n.a.	0.6	
	Tropical Atlantic		n.a.	0.7	
Northwest Pacific	1976 - 1979	n.a.	0.41	Tanabe and Tatsukawa, 1980	
Indian Ocean	1976	n.a.	0.1		
China sea	1977	n.a.	0.08		

786 n.s. not specified, n.a. not assessed

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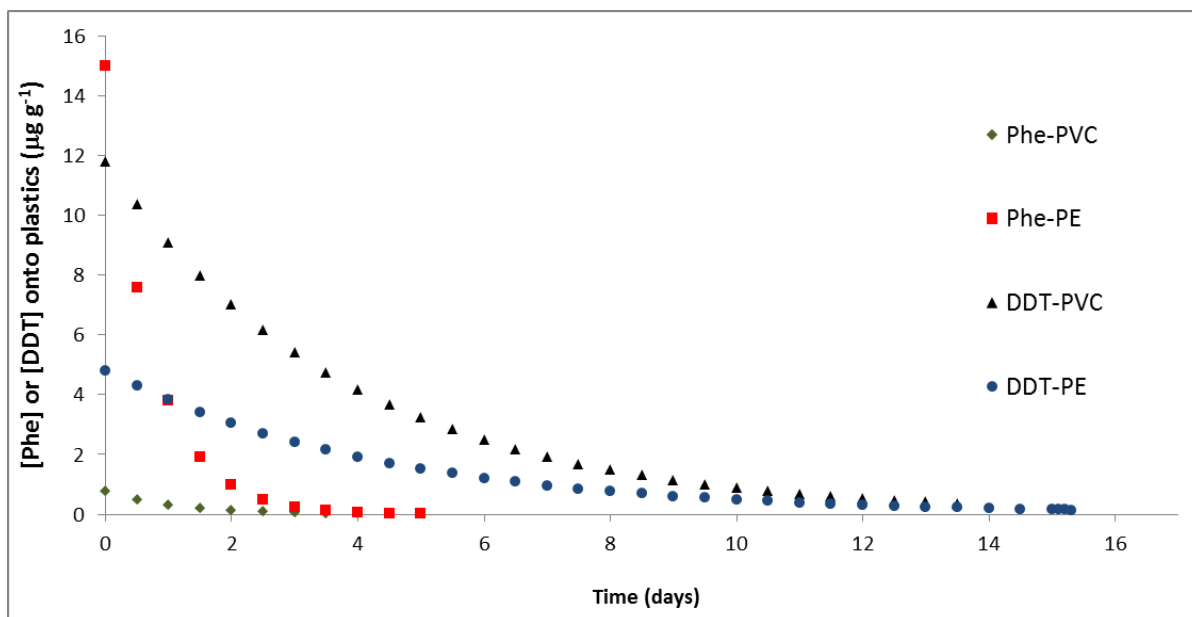
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794 *Desorption of sorbed contaminants*

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798 Fig.S10 Estimated time required for concentration of POPs onto plastics sorbed in estuaries to reach  
799 the concentration of sorbed POPs in marine waters.

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801 Table S6. Time required (in days) for estimated sorbed concentration of POPs onto plastics in  
802 estuaries to reach estimated concentration in marine waters

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POP/plastic	Time (days)
Phe-PVC	5
Phe-PE	5
DDT-PVC	13
DDT-PE	15

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