Transport of persistent organic pollutants by microplastics in estuarine conditions

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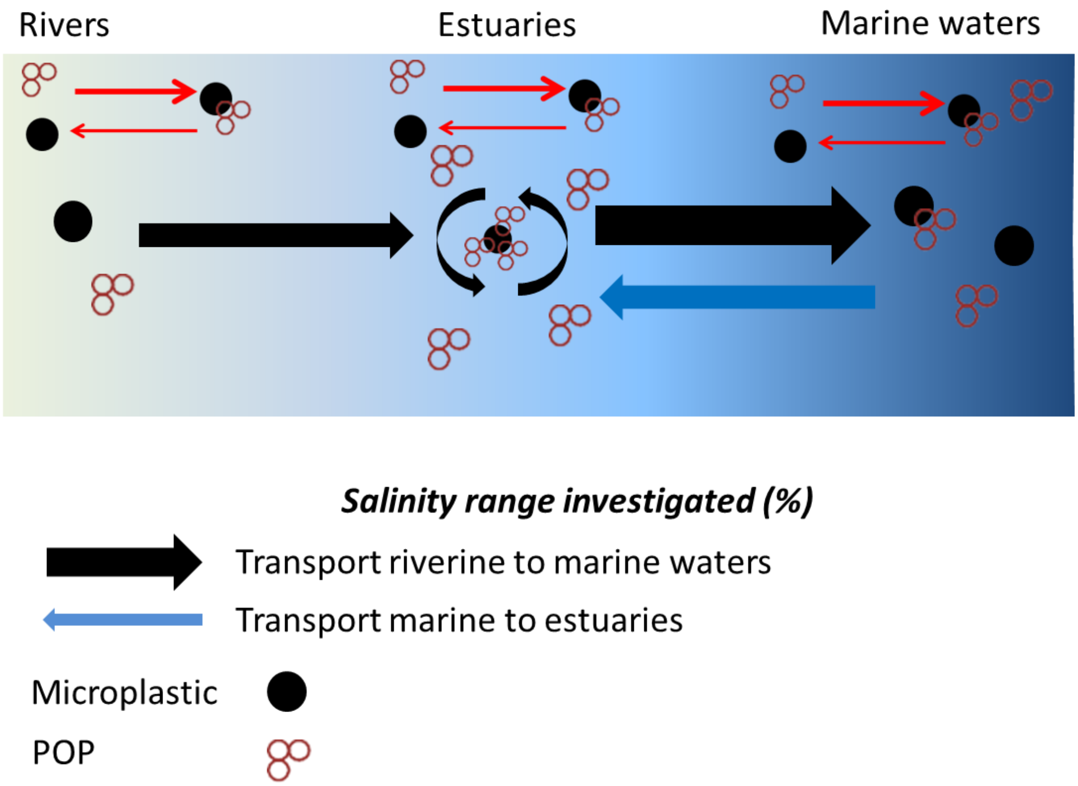
Highlights

- Salinity effect was investigated on sorption/desorption of POPs onto microplastics
- Little effect on sorption and no effect on their desorption rates was observed
- Transport of POPs will largely depend on their concentration in each ecosystem
- A transport model of POPs onto microplastics was proposed
- Transport followed the order: Phe-PE >> DDT-PVC = DDT-PE >> Phe-PVC

Graphical abstract



Abstract

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

Introduction

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

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

Browne et al. (2010) showed that microplastics were abundant in the intertidal zone in the Tamar estuary (UK) and Costa et al. (2011) showed that plastic debris is also found buried in estuarine sediments. Salinity, temperature and the presence of dissolved organic matter appear to be the main parameters governing the solubility of hydrophobic organic compounds such as POPs (Delle Site, 2001). Therefore, it is important to investigate the effects of each of these parameters on the sorption and desorption of POPs by microplastics. The assessment of sorption behaviour of POPs and their transport by microplastics is an important factor in their environmental risk assessment required to reach Good Environmental Status (GES) as part of the quality descriptor 10 of the Marine Strategy Framework Directive (MSFD 2008/56/EC). MSFD aims to establish "a framework within which Member States shall take the necessary measures to achieve or maintain GES in the marine environment by the year 2020".

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

Materials and methods

Sample preparation and characterisation

Unplasticised polyvinyl chloride (uPVC) and ultra high molecular weight (UHMW) polyethylene powder (Goodfellow, Huntington, UK) were sieved to the size range 200 – 250 μm to be representative of microplastics found in marine waters (Doyle, 2008; Thompson et al., 2004). PVC and PE were selected as plastics for study due to their widespread presence in the marine environment (Frias et al., 2010; Graham and Thompson, 2009; Ng and Obbard, 2006). Seawater was filtered (Whatman membrane filter cellulose nitrate 0.45 μm pore size) and autoclaved before use to reduce microbial activity and to remove any suspended particulate matter (SPM). The salinity range under investigation was 0, 25, 50, 75 and 100 % seawater corresponding to 0 (690 μS/cm), 8.8, 17.5, 26.3 and 35 psu (practical scale unit).

Sorption of phenanthrene and DDT to plastics

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

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

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

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

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

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

where q_e is the amount of contaminant sorbed onto plastic (μg kg^{-1}) at equilibrium and C_e is the contaminant concentration in the aqueous phase at equilibrium (μg L^{-1}).

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

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

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

Desorption of contaminants from plastic

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

Statistical analysis

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

Results and discussion

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

As model combinations, sorption equilibrium time of DDT onto PVC and Phe onto PE were investigated in seawater (35 psu) and in MilliQ water over a period of 15 days (Fig.1). Sorption equilibrium was reached in 24 hours and salinity was found to have no significant effect ($p > 0.01$ and $p = 0.229$ and $p = 0.601$) on sorption equilibrium time of Phe onto PE and DDT onto PVC respectively. This indicates that contaminants will reach equilibrium conditions onto plastics relatively quickly in freshwater, brackish or marine waters.

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

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

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

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

Desorption kinetics of contaminants from plastic

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

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

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

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

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

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

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

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

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

$$C = C_0 \exp(-kt) \qquad \text{Eq. [3]}$$

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

The results indicated that 5 days were required for the concentration of Phe sorbed onto PVC and PE in estuaries to desorb and reach concentration estimated in marine waters (Fig.4). A much longer timescale was required for DDT desorption from plastics with 13 and 15 days for PVC and PE respectively. The potential for microplastics to transport pollutants from estuaries will therefore be dependent on the estuary's cycle including flushing and particle residence time. Jay et al. (1997) characterised the particle residence time for some estuaries for different locations. Timescales varied from 3 to 9 months for Chesapeake Bay to 0.5 day for Plum Island Sound (Jay et al., 1997). For estuaries presenting a short particle retention time, microplastics are therefore likely to act as vectors for transport of Phe and DDT to marine waters but with limited exposure to organisms. For estuaries with longer retention time, such as Chesapeake Bay, desorption of POPs from plastics could be of concern as well as the exposure of contaminated particles to aquatic organisms. It is however unknown whether the contaminants sorbed onto plastics can then desorb upon ingestion by marine organisms at concentrations which may cause significant harm or ecologically adverse effects. Microplastic ingestion has been documented for a wide range of organisms at many trophic levels (Avery-Gomm et al., 2012; Besseling et al., 2012; Blight and Burger, 1997; Boerger et al., 2010; Bravo Rebolledo et al.; Browne et al., 2008; Day, 1980; Denuncio et al., 2011; Lusher et al., 2013) with some evidence of trophic transfer of plastics (Farrell and Nelson, 2013). Transfer of sorbed contaminants from plastic following ingestion has also been suggested (Tanaka et al., 2013). As estuaries are the most productive ecosystems in the marine environment and due to the relatively long particle retention time in such systems; it is highly likely that a wide range of marine organisms are exposed to contaminated microplastics, but the chemical effects, if any, of this are unknown. Microplastics can enter the marine environment through land-based sources and are exposed to POPs from anthropogenic sources, where sorption takes place. Contaminated particles are then transported into estuaries where they can reside for a relatively long time, depending on the type of estuary. Contaminated particles can also settle, accumulate or being buried onto sediments as well as being deposited on the shoreline (Browne et al., 2011; Browne et al., 2010). Man-made operations involving the suspension of sediments, such as dredging, could cause a large release of contaminated particles into the marine environment.

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

Conclusions

Increases in salinity had no significant effects on the sorption capacity of PVC and PE for Phe; however sorption capacity for DDT was significantly higher in the absence of salinity suggesting a differential mechanism of sorption for contaminants. The transport capacity of these plastics for DDT and Phe in estuaries will likely be more related to the aqueous concentration of the contaminants than to the salinity. The transport model proposed showed that the amount of POPs sorbed by plastics in freshwater, to brackish and marine waters followed the order: Phe-PE >> DDT-PVC = DDT-PE >> Phe-PVC. Microplastics have the potential to sorb substantially more contaminants in estuaries due to higher reported concentrations of contaminants than in riverine and marine waters. Sorption equilibrium of POPs onto microplastics is also expected to be reached in each system due to their long particle residence and potential storage in estuarine sediments. As desorption rates of sorbed contaminants were not affected by salinity, amounts desorbed are expected to be correlated to the particle retention time in estuaries and marine waters. The proposed transport model suggested that estuaries can represent an important source for contaminated microplastics with their pulse release to the marine environment through natural (e.g. flushing) and anthropogenic processes (e.g. dredging).

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

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Figures

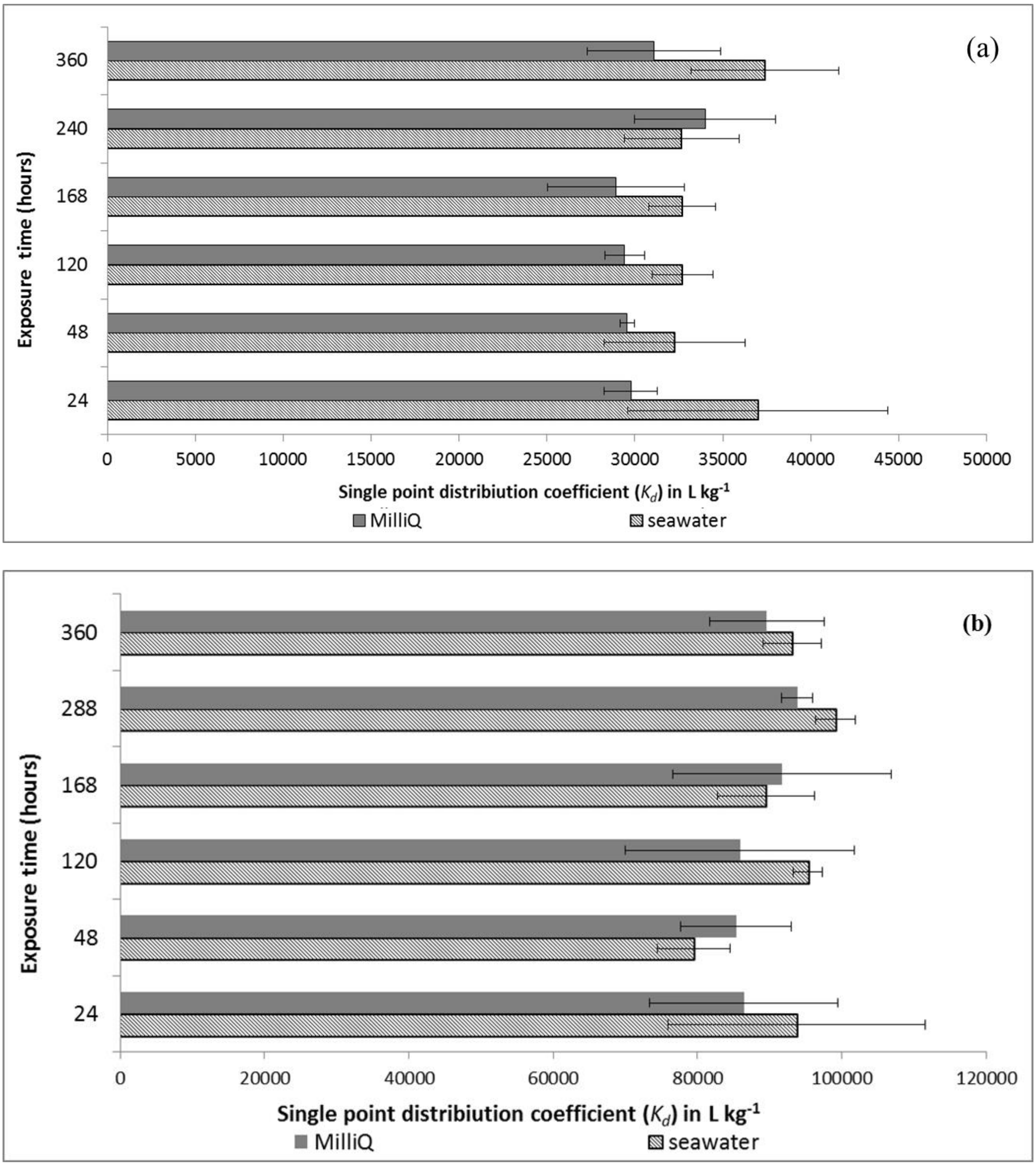


Fig.1 Sorption equilibrium time of (a) Phe onto PE and (b) DDT sorption onto PVC in seawater (35 psu) and in MilliQ water (n = 3, ± SD).

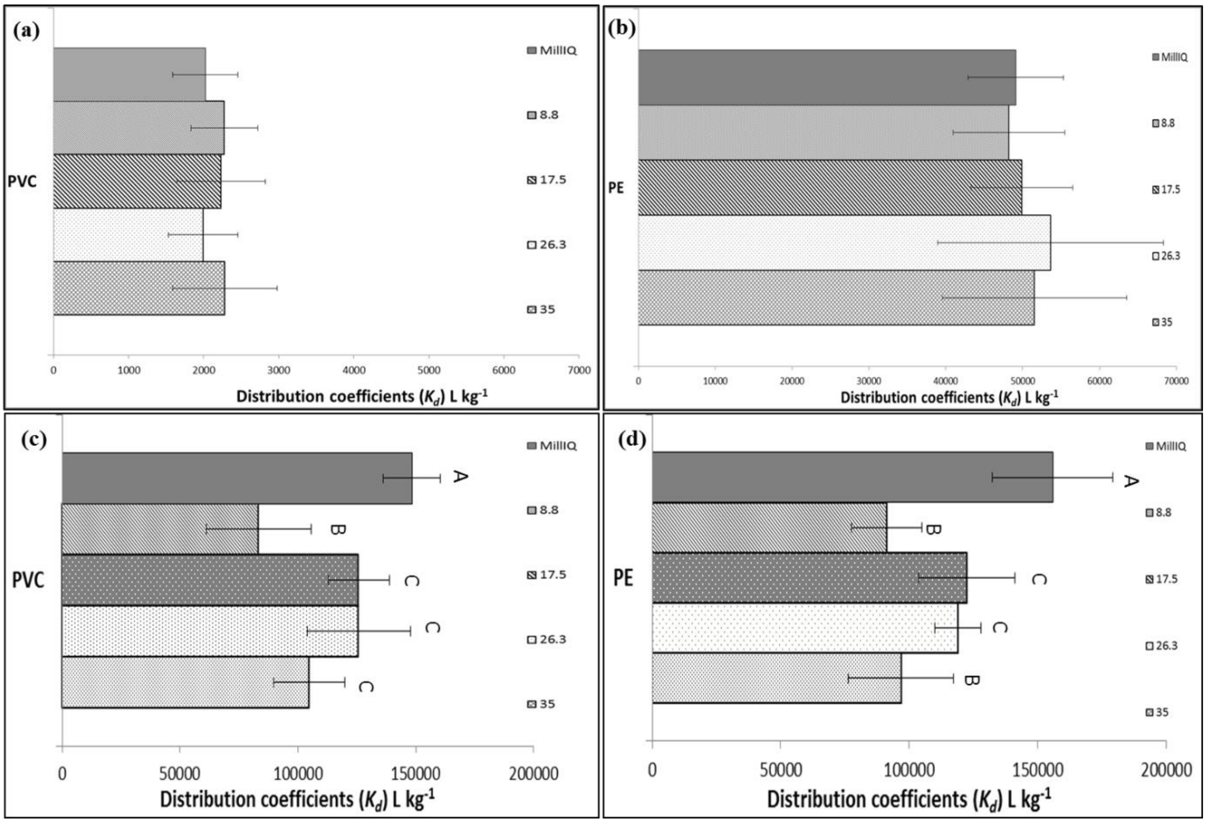


Fig.2 Distribution coefficients (K_d) calculated from the sorption of Phe onto (a) PVC, Phe onto (b) PE, DDT onto (c) PVC and DDT onto (d) PE for different salinities (n = 3, ± SD). (A, B, C: no significant differences between K_d values; $p < 0.01$).

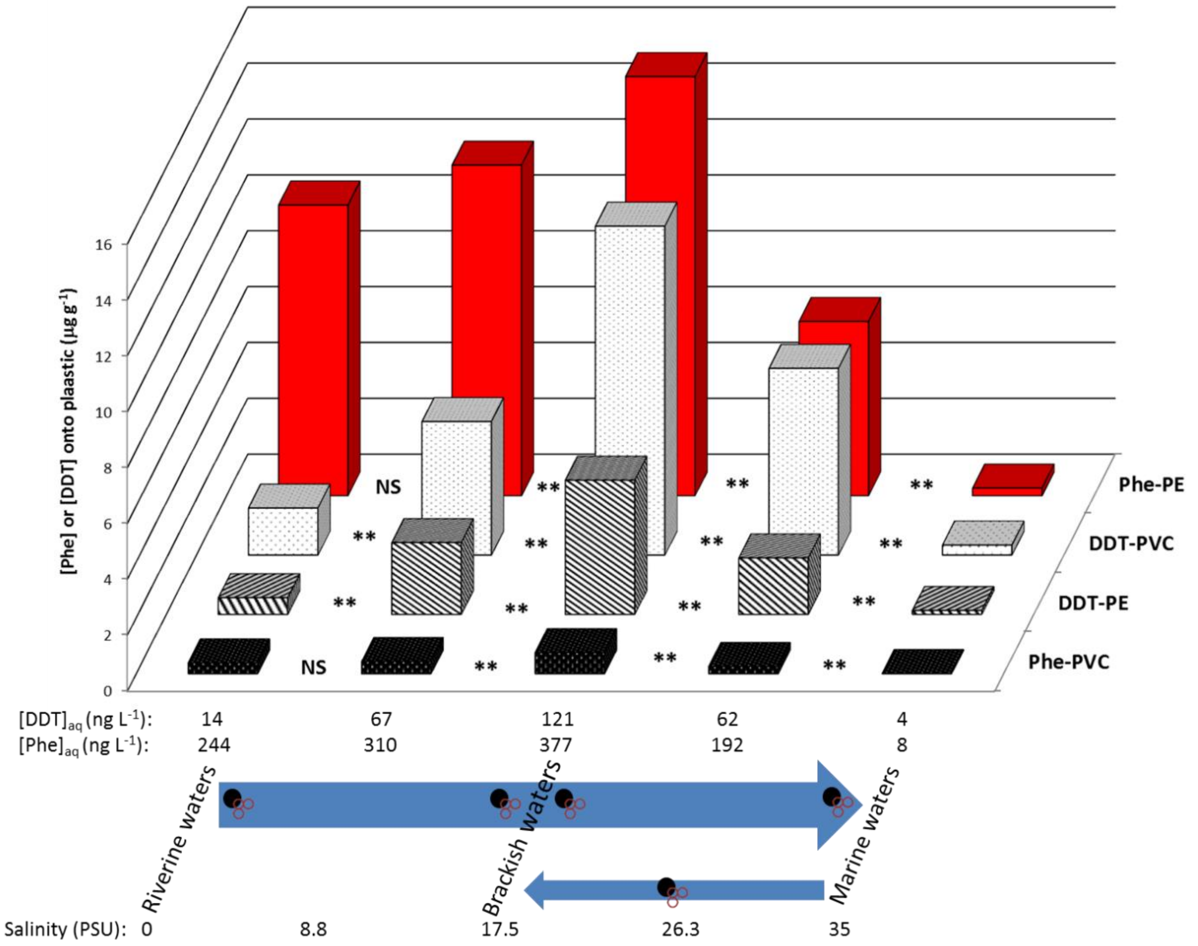


Fig.3 Potential for microplastics to sorb and transport phenanthrene (Phe) and DDT in riverine, estuarine and marine waters according to reported typical environmental concentrations of Phe and DDT. Calculated amounts sorbed onto plastics via K_d values measured herein. Statistics analysis carried-out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

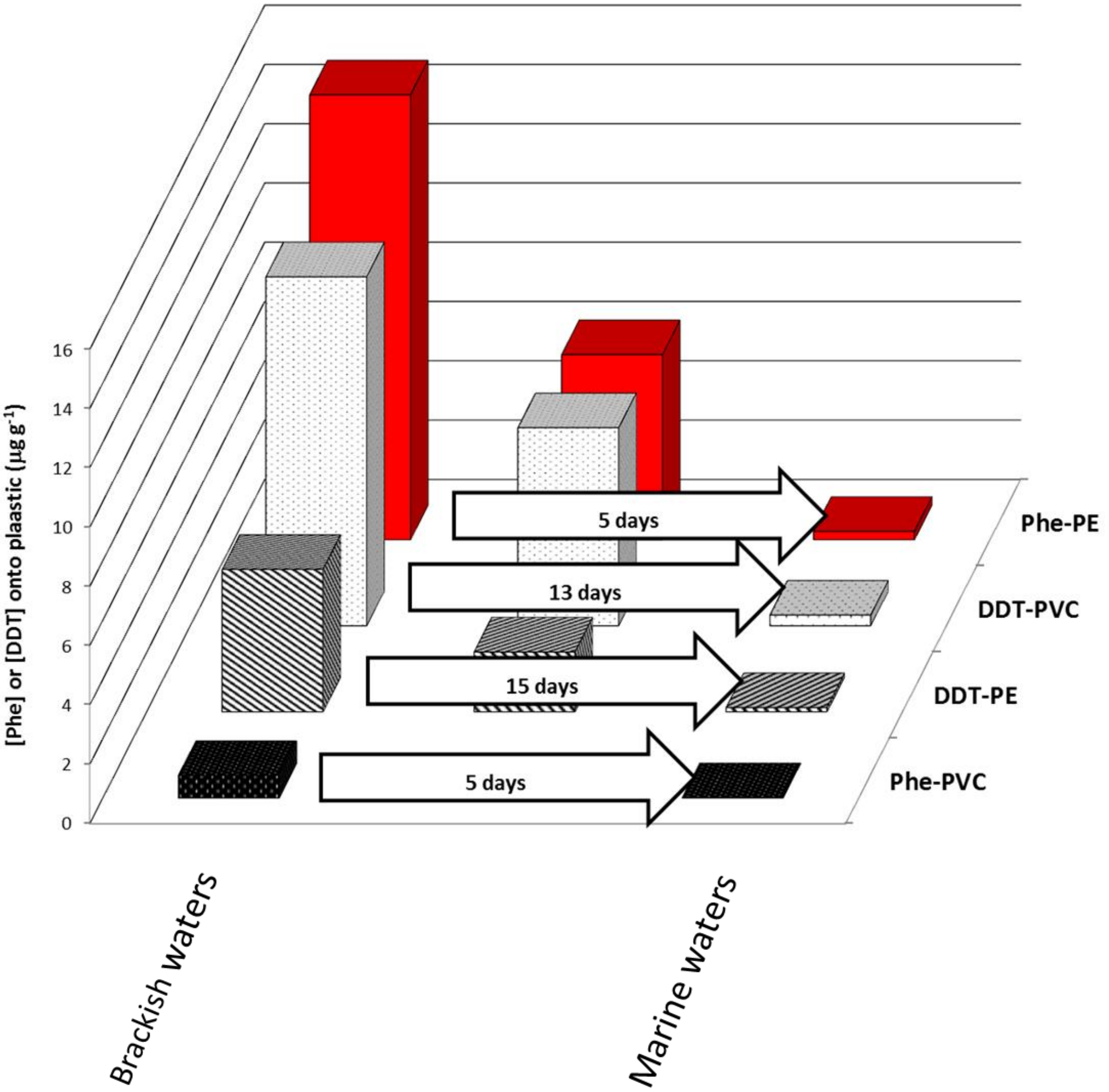


Fig. 4 Time required (in days) for contaminants sorbed onto plastics in estuaries to reach concentration of estimated sorbed contaminants onto plastics in marine waters.

Tables

Table 1. Pollutants under investigation and associated parameters.

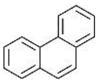
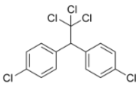
Pollutant	Chemical structure	Initial concentration ($\mu g\ L^{-1}$)	Specific activity (MBq/mmol)	Supplier	Solvent	MW ($g\ mol^{-1}$)	Distilled water	Log Kow
^{14}C-Phe		0.6-6.1	303.4	Sigma-Aldrich	Methanol	178.23	600 (22°C) (EPA, 2013)	4.5 (MacKay et al. (1993))
^{14}C-DDT		0.8-3.1	370-110	ARC, Inc.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

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

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

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

Plastic	pollutant	Aqueous solution (salinity, PSU)	Desorption rate (k, day^{-1} ± SD)
PVC	Phe	MilliQ (0)	0.73 ± 0.26
		Seawater (35)	0.88 ± 0.56
PE		MilliQ (0)	1.15 ± 0.12
		Seawater (35)	1.37 ± 0.45
PVC	DDT	MilliQ (0)	0.21 ± 0.01
		Seawater (35)	0.26 ± 0.06
PE		MilliQ (0)	0.20 ± 0.04
		Seawater (35)	0.23 ± 0.08

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

Ecosystems	Contaminant concentration (ng L^{-1})	
	Phe	DDT
Rivers	243.68	13.97
Estuaries	**377.25**	**120.78**
Marine waters	7.5	3.83

Transport of persistent organic pollutants by microplastics in estuarine conditions

Supplementary information

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Recovery of contaminants

Table S1. Total recovery (%) of the contaminants (radioactivity) and recovery in each phase (A: aqueous phase, G: glass walls, S: solid phase, T: total) (averaged values, n=12)

	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	**81**	2	3	86	**91**	2	3	72	**77**	3	2	82	**87**	2	1	80	**83**
DDT-PE	2	3	84	**89**	2	3	86	**91**	2	3	72	**77**	3	2	82	**87**	2	1	83	**86**
Phe-PVC	51	2	43	**96**	51	2	45	**98**	53	2	48	**103**	54	2	43	**99**	46	1	40	**87**
Phe-PE	4	3	77	**84**	4	6	72	**82**	46	1	38	**85**	4	6	73	**83**	3	8	81	**92**

Sorption equilibrium time

Statistical analysis

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

(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			

(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			

Binding sorption isotherms

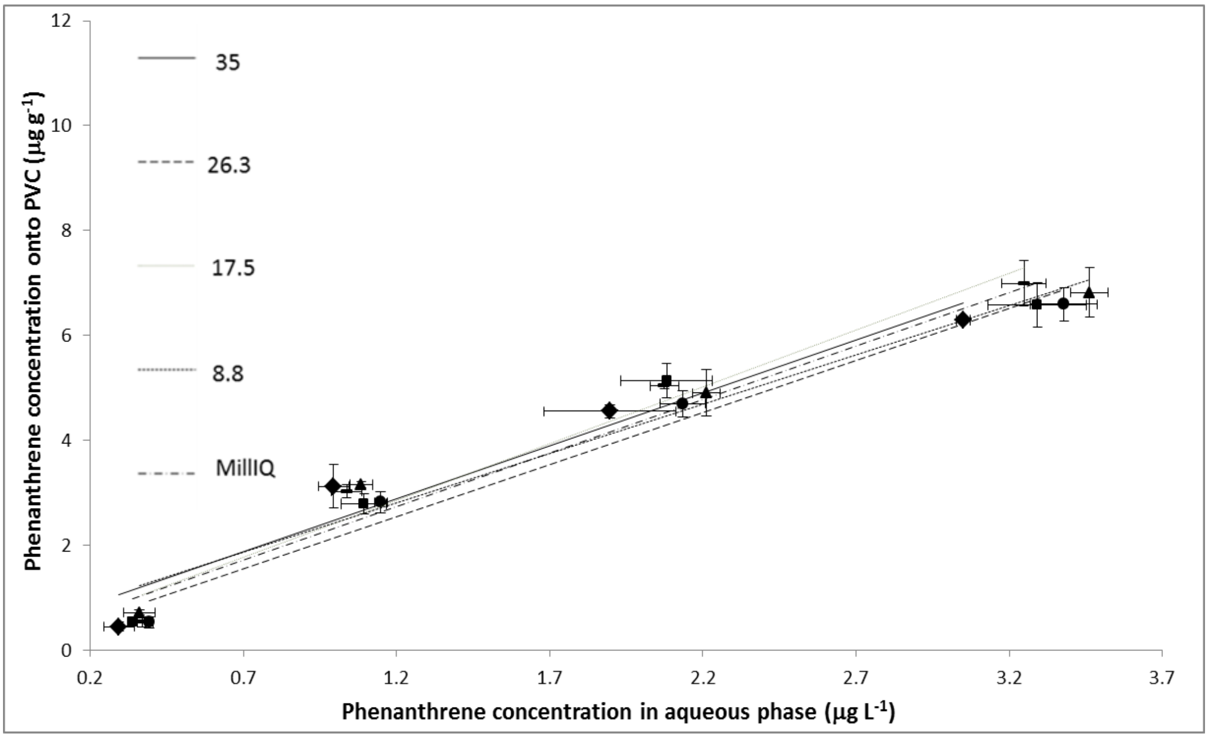


Fig.S1 Sorption isotherms of phenanthrene (Phe) sorption onto PVC for different salinities (n = 3, ± SD).

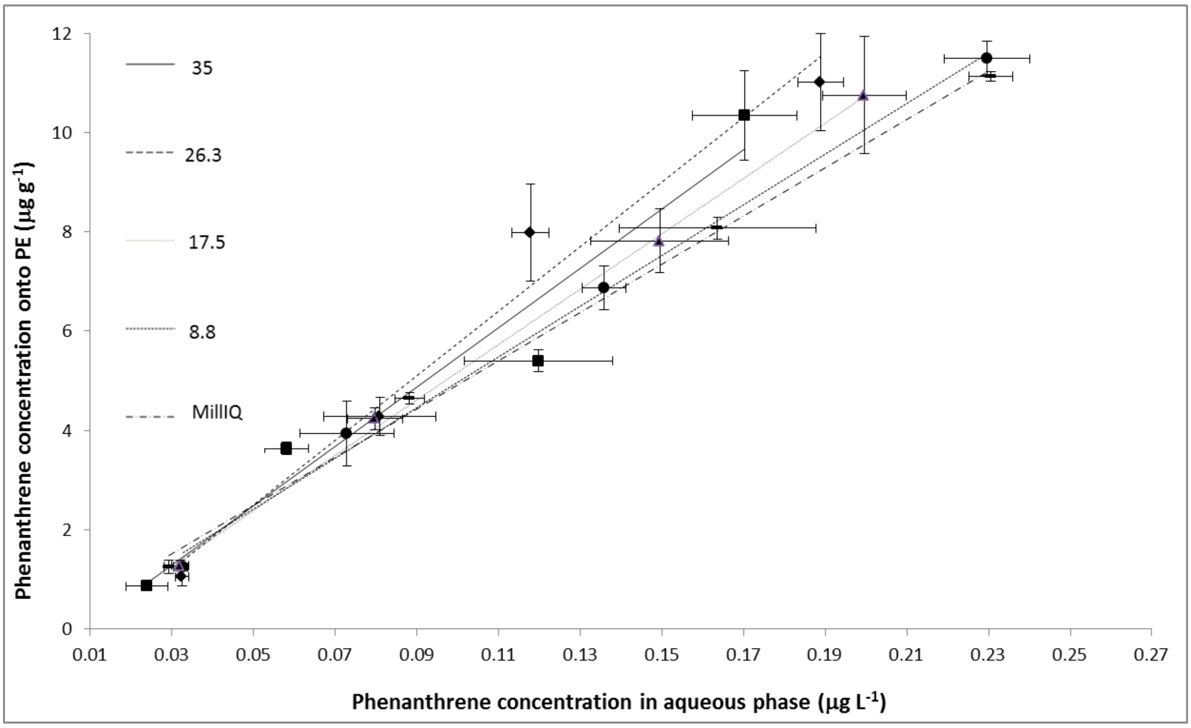


Fig.S2 Sorption isotherms of phenanthrene (Phe) sorption onto PE for different salinities (n = 3, ± SD).

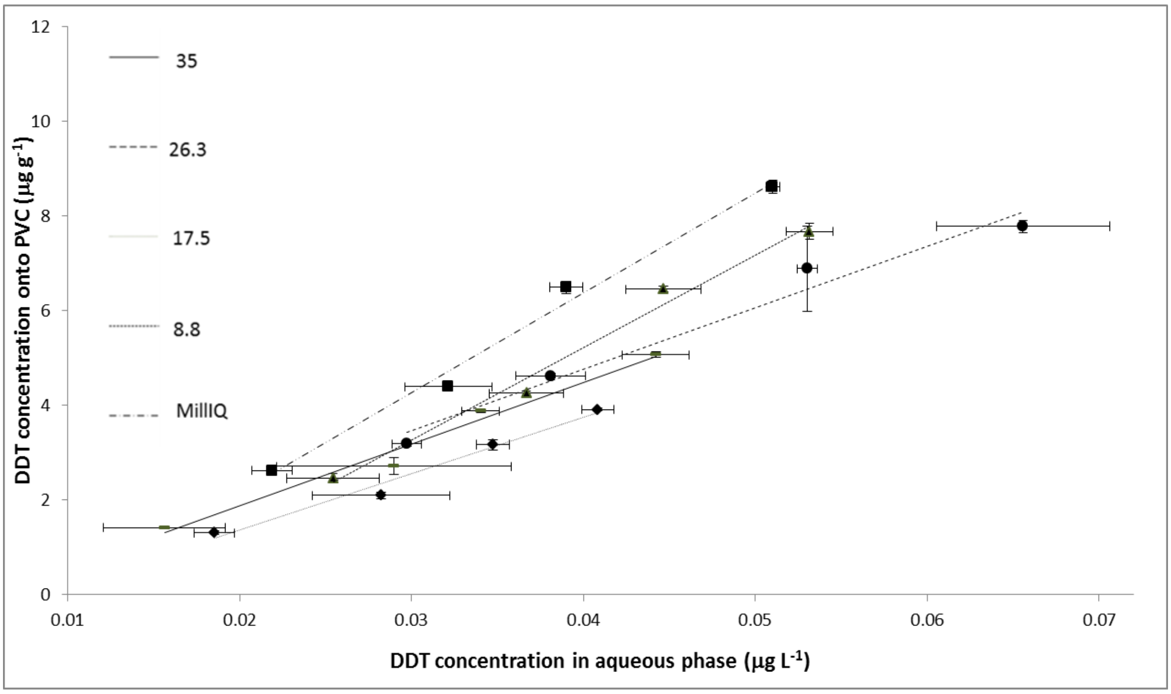


Fig.S3 Sorption isotherms of DDT sorption onto PVC for different salinities (n = 3, ± SD).

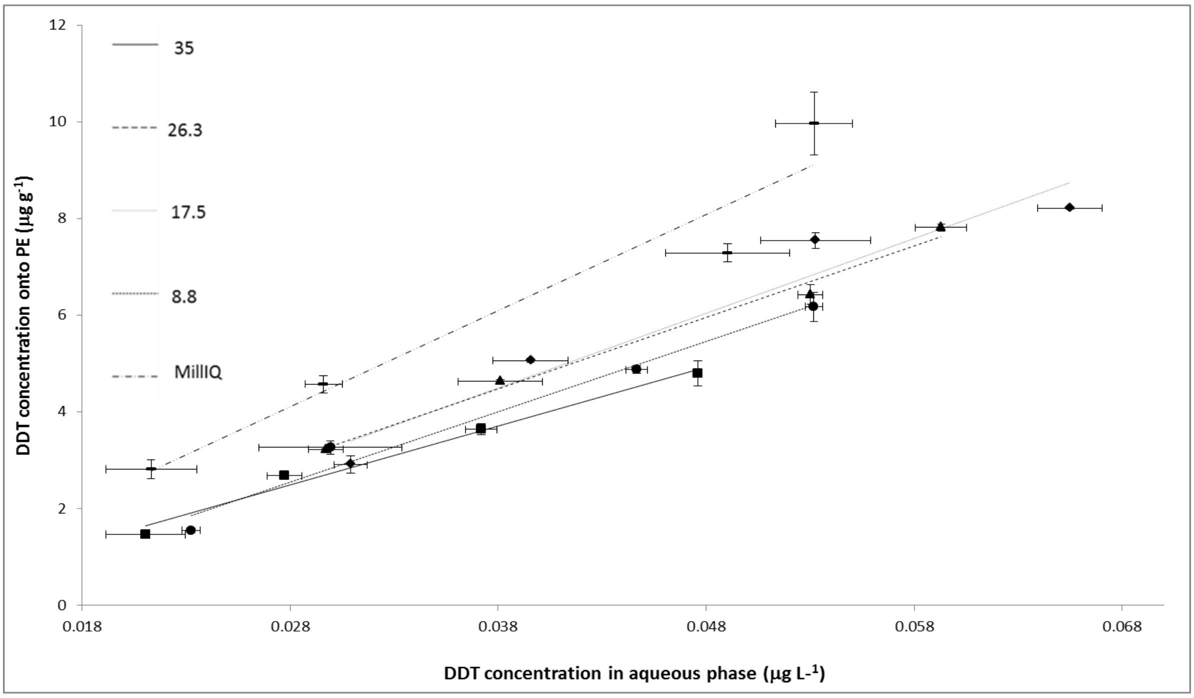
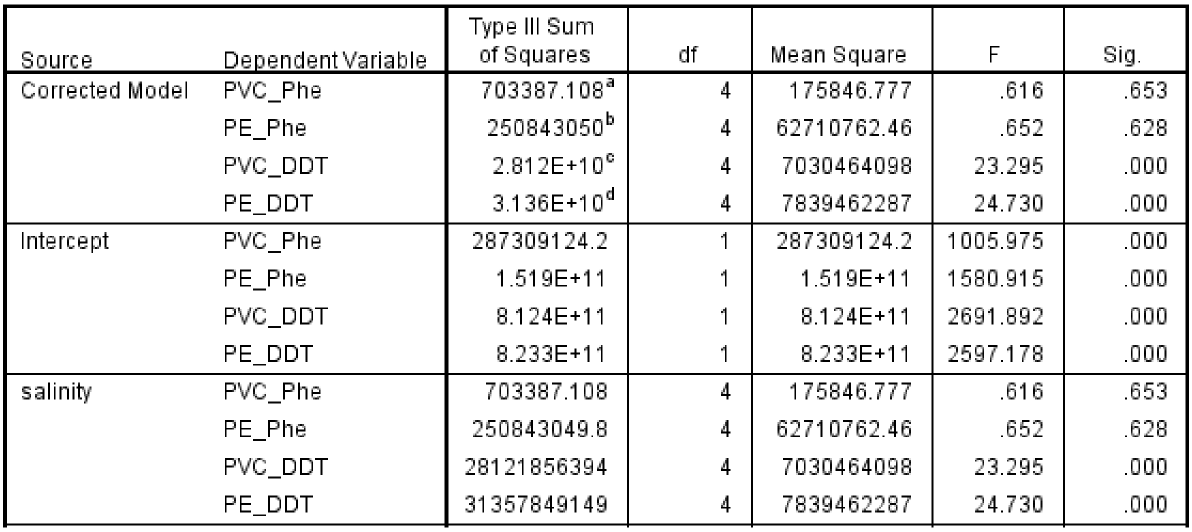


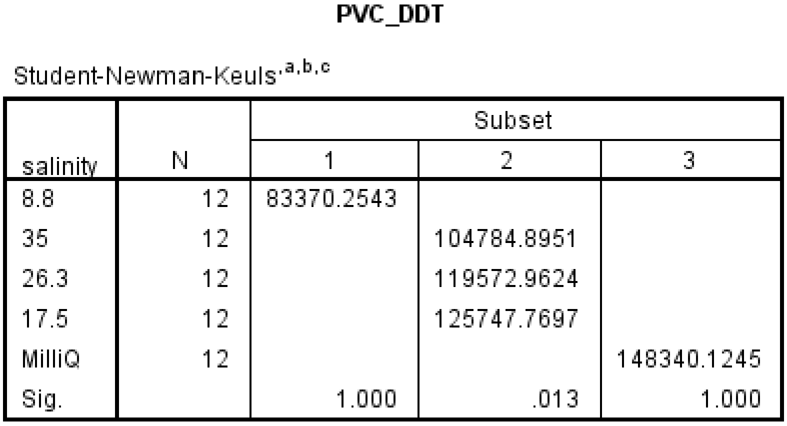
Fig.S4 Sorption isotherms of DDT sorption onto PE for different salinities (n = 3, ± SD).

Statistical analysis

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



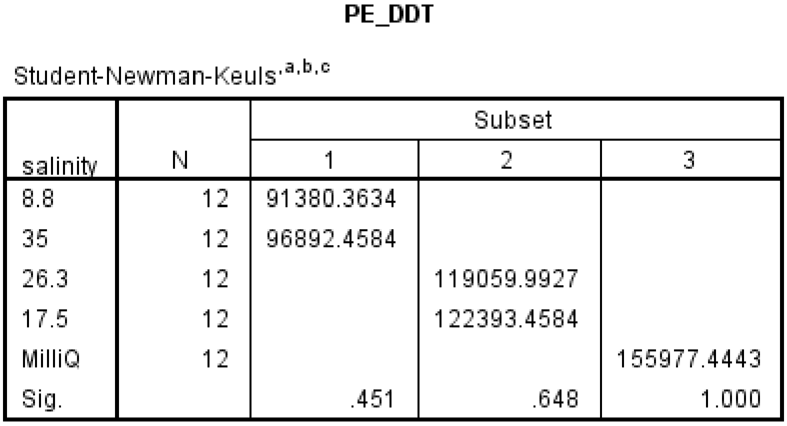
Source	Dependent Variable	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	PVC_Phe	703387.108[a]	4	175846.777	.616	.653
	PE_Phe	250843050[b]	4	62710762.46	.652	.628
	PVC_DDT	2.812E+10[c]	4	7030464098	23.295	.000
	PE_DDT	3.136E+10[d]	4	7839462287	24.730	.000
Intercept	PVC_Phe	287309124.2	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



PVC_DDT

Student-Newman-Keuls[a,b,c]

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



PE_DDT

Student-Newman-Keuls[a,b,c]

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

Freundlich binding sorption isotherms

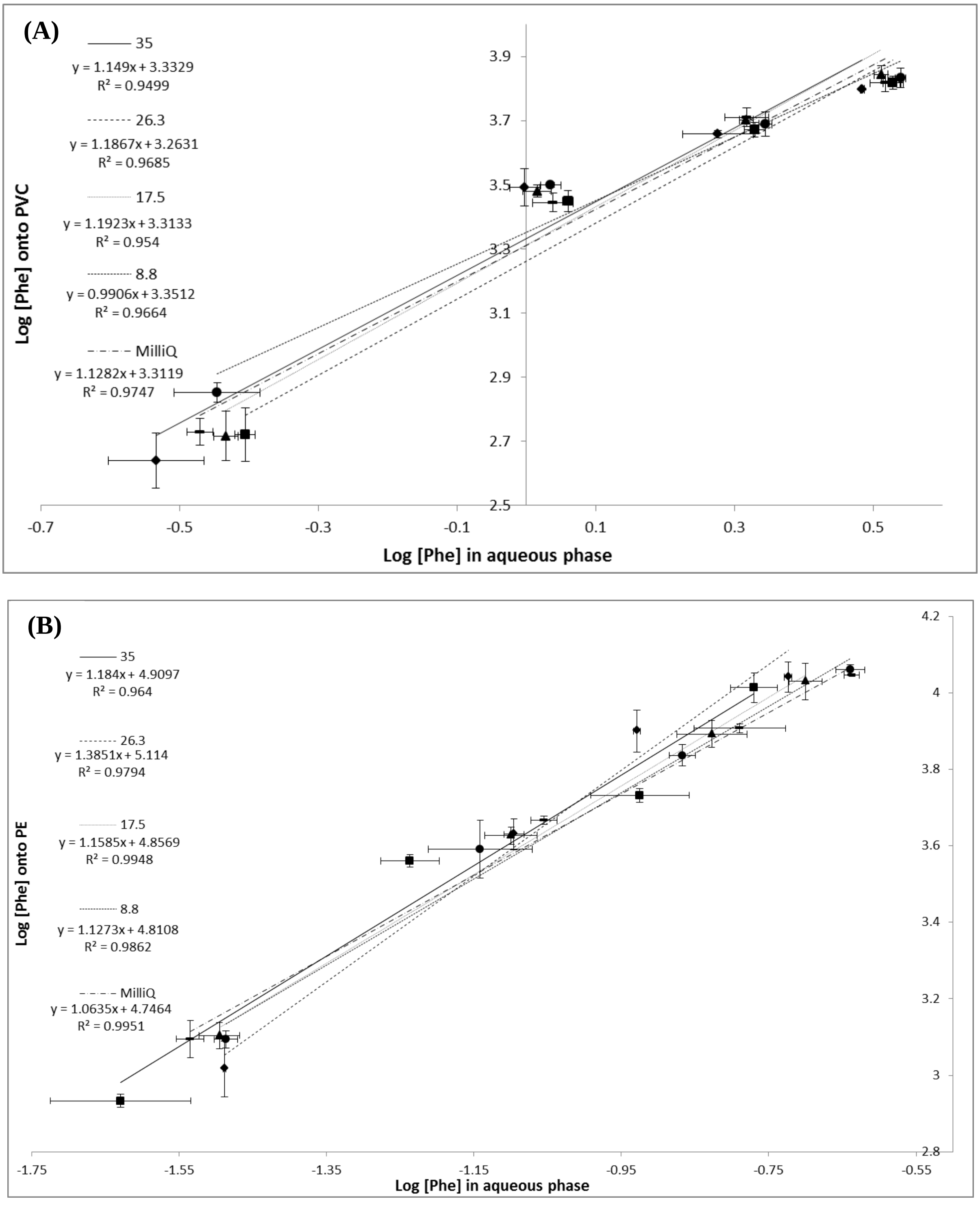


Fig.S5 Freundlich binding sorption isotherms for phenanthrene (Phe) sorption onto (A) PVC and (B) PE (n = 3, ± SD).

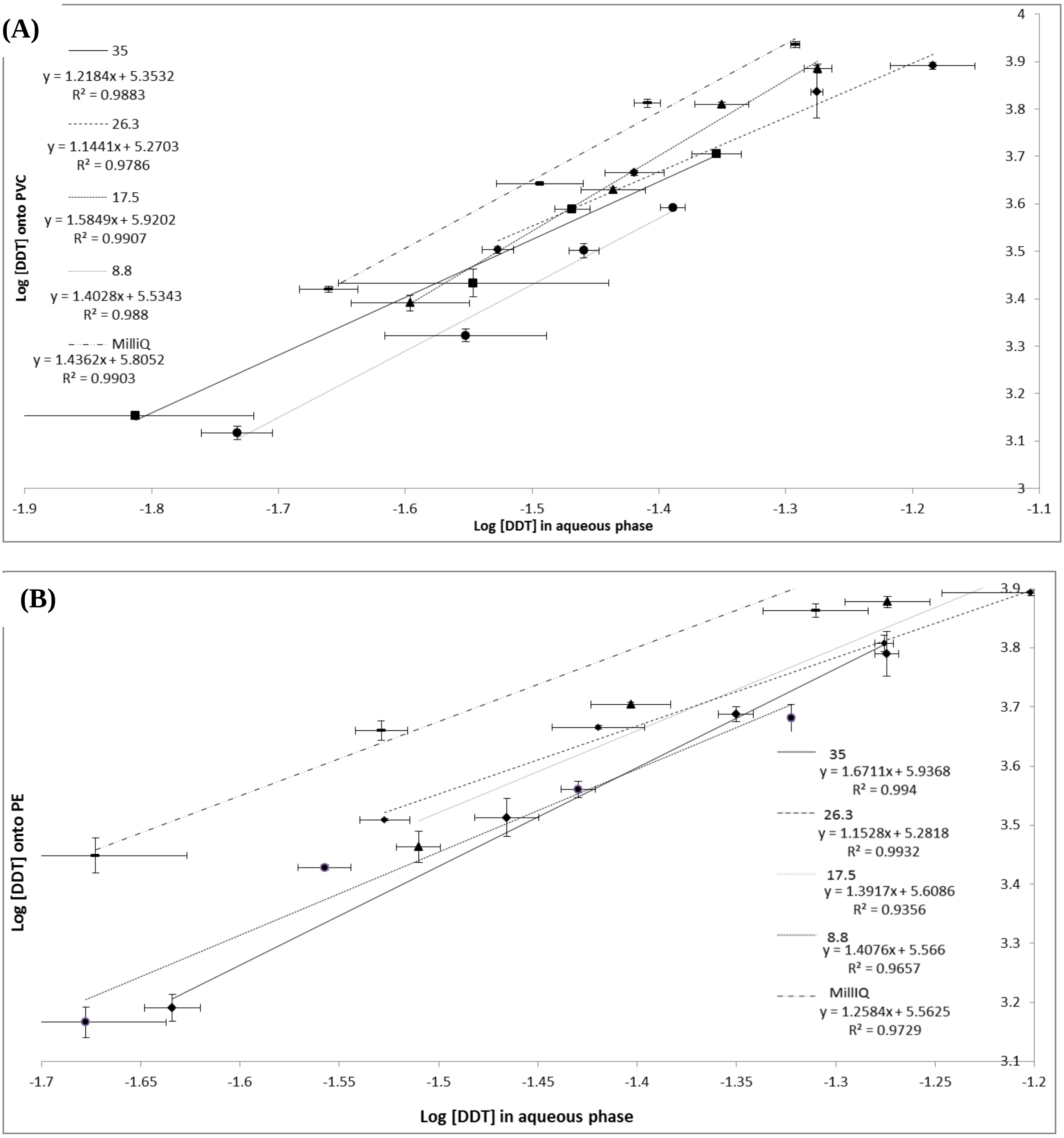


Fig.S6 Freundlich binding sorption isotherms for DDT sorption onto (A) PVC and (B) PE (n = 3, ± SD).

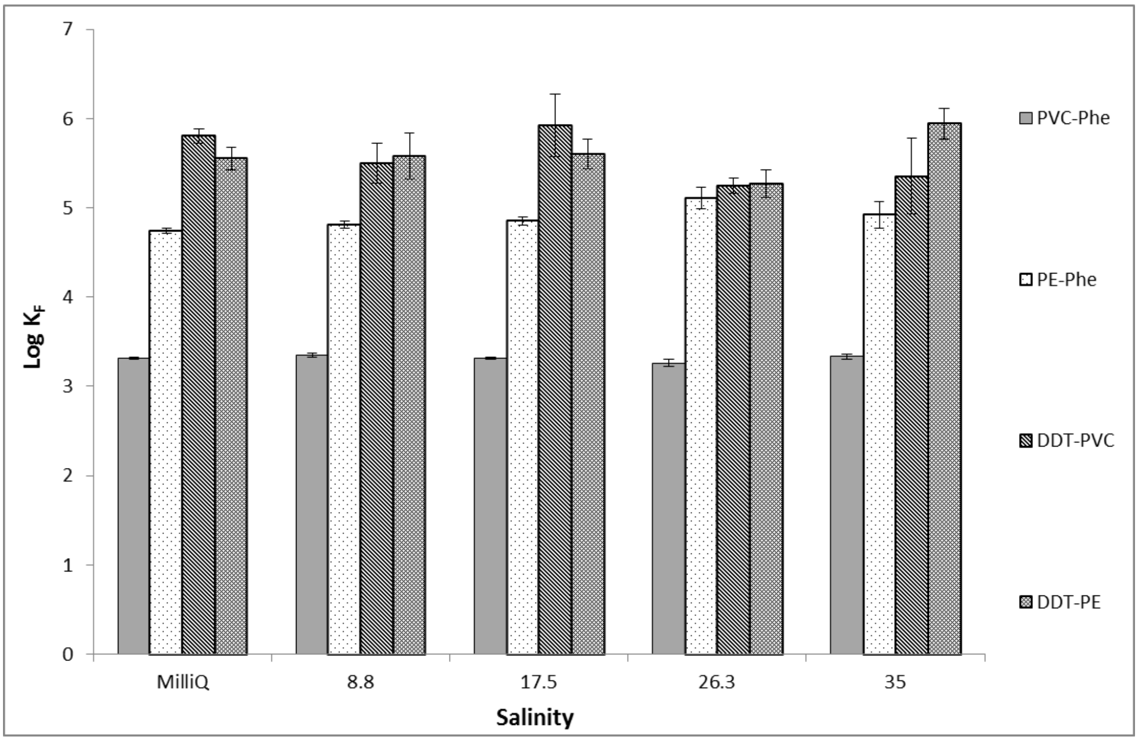


Fig. S7 Log KF values as a function of salinity for Phe and DDT sorption onto PVC and PE (n = 3, ± SD)

Desorption of contaminants from plastic

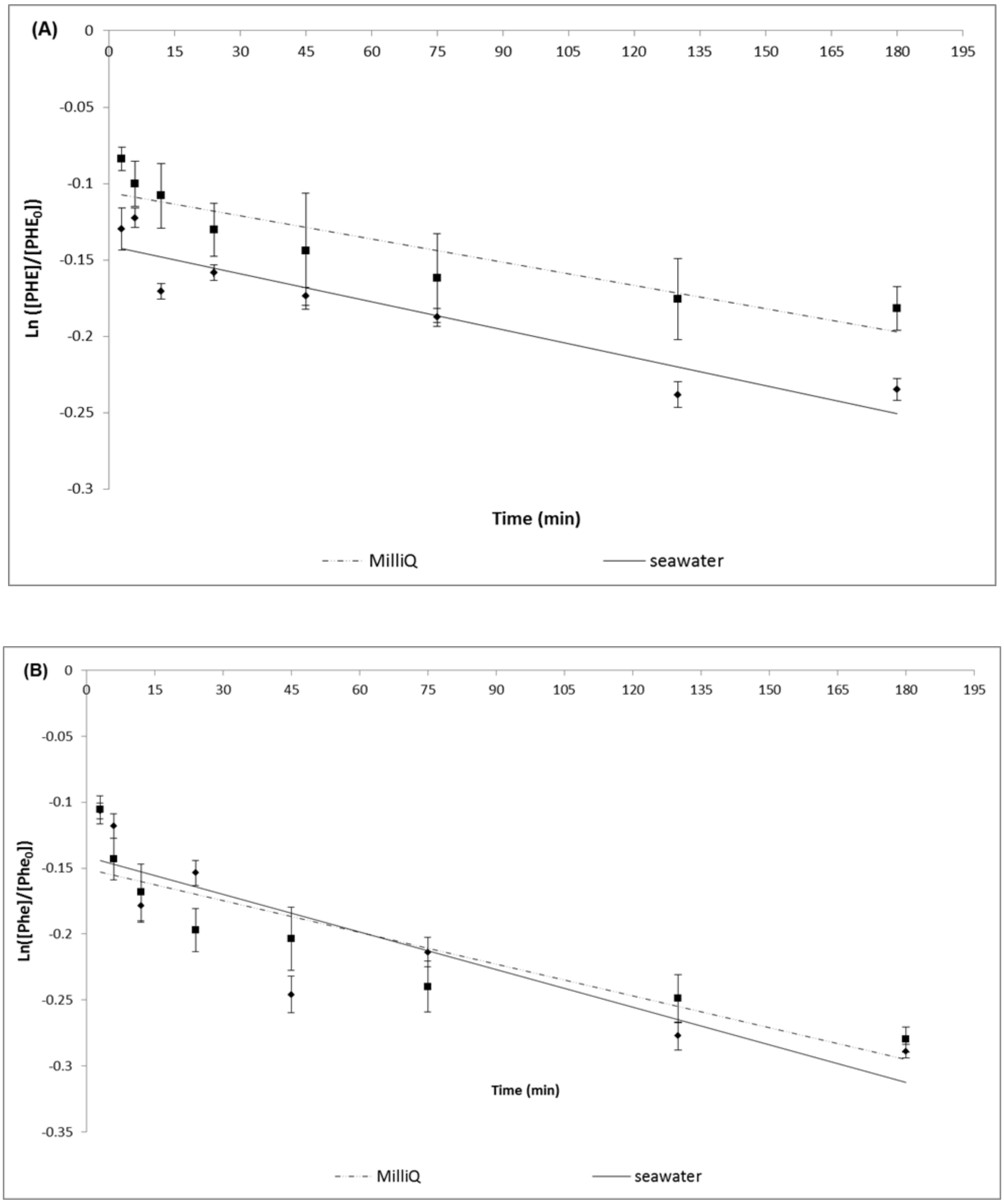


Fig.S8 Desorption kinetics of phenanthrene (Phe) from (A) PVC and (B) PE in in MilliQ and in seawater (35 psu) (n = 3, ± SD).

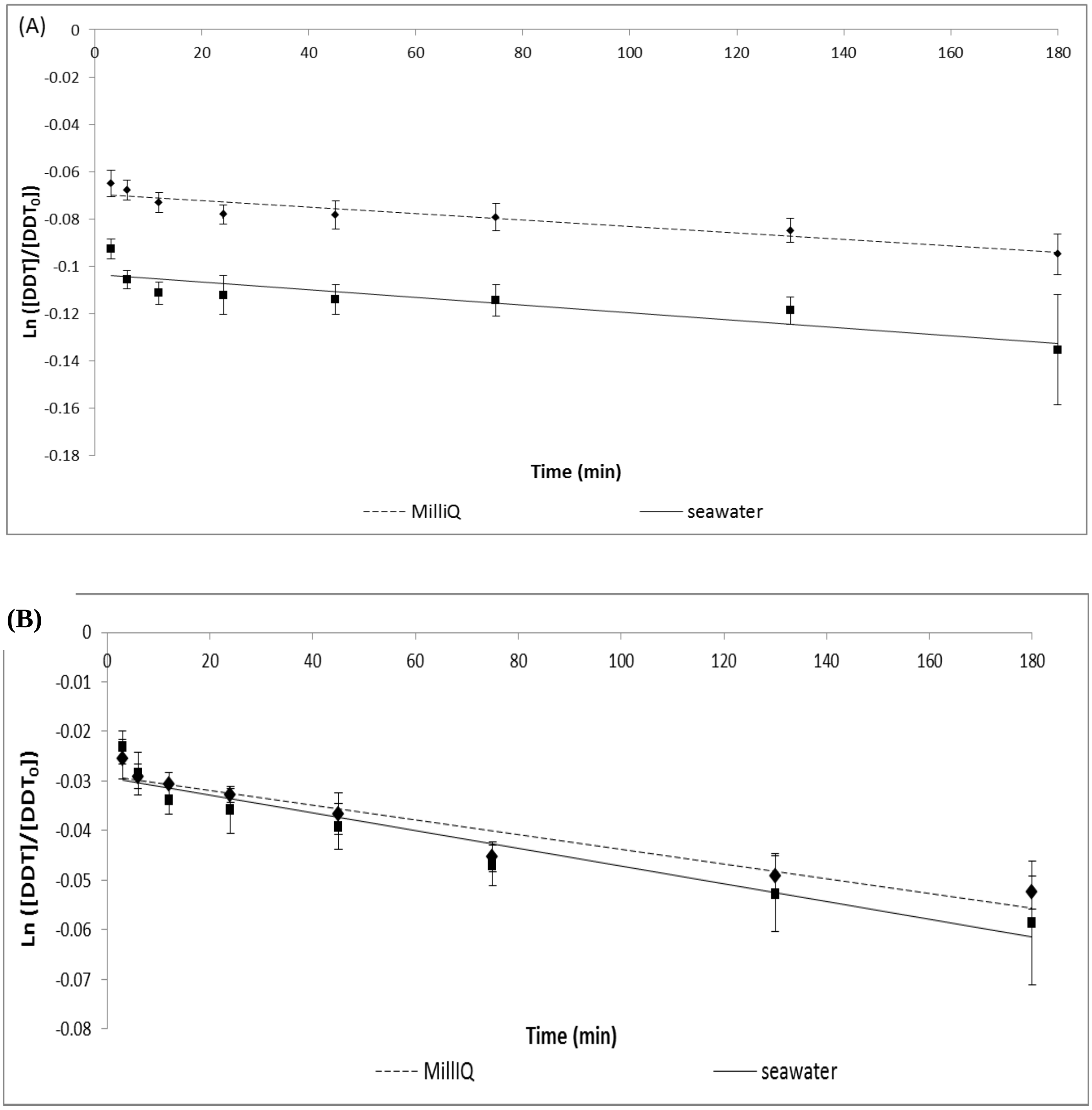


Fig.S9 Desorption kinetics of DDT from (A) PVC and (B) PE in MilliQ and in seawater (35 psu) (n = 3, ± SD).

Statistical analysis

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

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			

Environmental significance

Transport of POPs in estuaries

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

	Location	**Sampling time**	**Phe**	**∑ DDT**	**References**
River	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
	Liaohe 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
Estuaries	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.	Pérrez-Carrera et al., 2007
Marine	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	
	Subarctic Atlantic		n.a.	0.6	Orlova et al., 1983
	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	

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

Desorption of sorbed contaminants

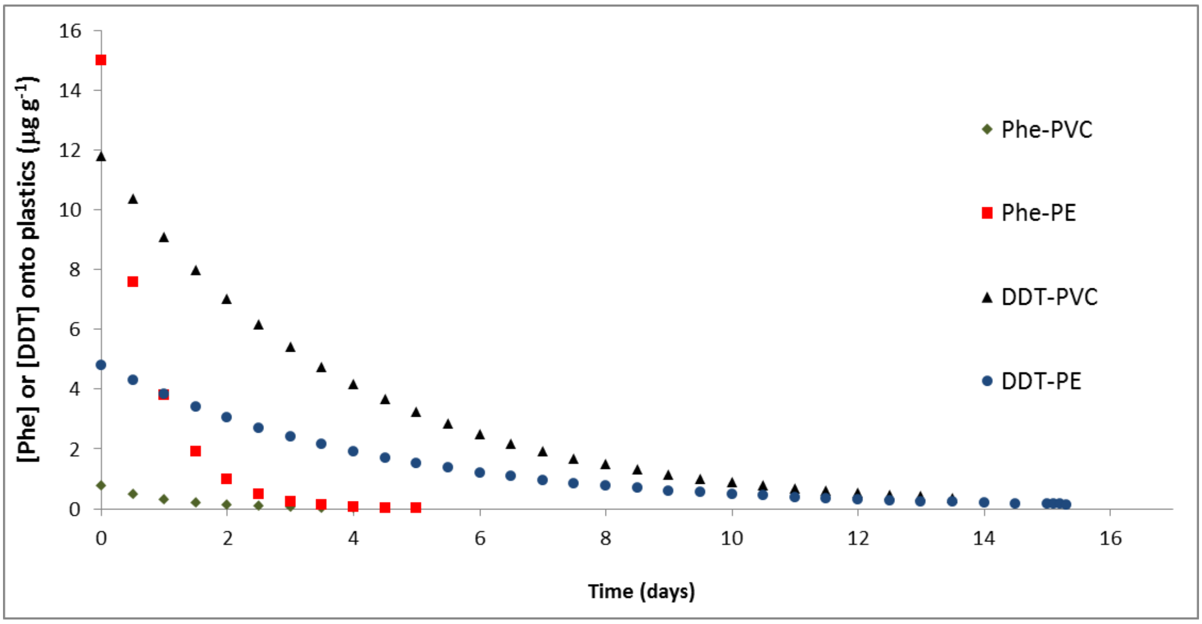


Fig.S10 Estimated time required for concentration of POPs onto plastics sorbed in estuaries to reach the concentration of sorbed POPs in marine waters.

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

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