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Transport of persistent organic pollutants by microplastics in estuarine conditions

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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 polyvinyl chloride (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.

1. 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. Most 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 (Fendall and Sewell, 2009; Browne et al., 2011). There is evidence that the abundance of microplastics is increasing in the marine environment (Thompson et al., 2004; Doyle et al., 2011) 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., 2014) of

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ingestion of microplastics. Microplastics can accumulate in the digestive gland of marine bivalves and microplastics (<9.6 μm) were shown 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 European 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 (Ng and Obbard, 2006; Graham and Thompson, 2009; Thompson et al., 2009; Frias et al., 2010; Browne et al., 2011), 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.

2. Materials and methods

2.1. 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 (Thompson et al., 2004; Doyle, 2008). PVC and PE were selected as plastics for study due to their widespread presence in the marine environment (Ng and Obbard, 2006; Graham and Thompson, 2009; Frias et al., 2010). 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 salinity scale unit).

2.2. Sorption of phenanthrene and DDT to plastics

Analysis of samples over a period of 360 h showed that equilibrium concentrations in seawater and on the plastic were reached after 24 h (Bakir et al., 2014). Equilibrium sorption time of POPs onto plastics in MilliQ only was also investigated over a period of 360 h. 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 h 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:

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

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).

$$\log q_e = \log K_F + 1/n_F \log C_e \quad (2)$$

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