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Uptake and Release Kinetics of Organic Contaminants Associated with Micro- and Nano- Plastic Particles

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Abstract

A generic theoretical framework is presented for describing the kinetics of uptake and release of organic compounds that associate with plastic particles. The underlying concepts account for the physicochemical features of the target organic compounds and the plastic particles. The developed framework builds on concepts established for dynamic speciation analysis by solid-phase microextraction (SPME), and the size-dependent reactivity features of particulate complexants. The theoretical framework is applied to interpretation of literature data, thereby providing more rigorous insights into previous observations. The presented concepts enable predictions of the sink/source functioning of plastic particles and their impact on the dynamic chemical speciation of organic compounds in aqueous environmental media and within biota. Our results highlight the fundamental influence of particle size on the uptake and release kinetics. The findings call for a comprehensive description of the physicochemical features of plastic particles to be provided in experimental studies on micro- and nano-plastics in different types of aquatic environmental media.

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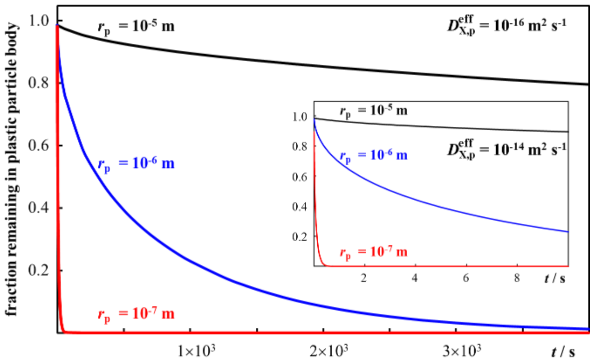

Introduction

The environmental impact of plastic particles is a current focus of intense international research efforts. Sorting out the potential adverse effects of plastic particles on biota is a challenging task on many levels. Plastic materials are complex chemical mixtures: they contain a range of polymer additives which are included to confer favorable properties such as plasticity, UV resistance, flame resistance; monomers and intermediate synthetic products may also be present.[1,2] During the product lifetime, additives, monomers, and other compounds that are mobile in the bulk polymer matrix may migrate and be released into the environment and food chains.[3] The extent and timescale of such release depends on a number of factors including the affinity of the compounds for the polymer backbone, the diffusion coefficient of the compound in the polymer phase, the surface area and volume of the plastic particle, as well as the concentration gradient at the particle/medium interface, which in turn may be affected by the pH and ionic strength of the aqueous medium.[4] Once plastic materials enter aquatic environments, their associated organic contaminant load will derive from the uptake/release kinetics of the compounds initially present and of the suite of diverse compounds present in the ambient surroundings. Microplastics (MPs) collected from a range of environmental settings worldwide are found to have sorbed a wide range of metal species and organic contaminants from their surroundings;[5-,6,7,8,9,10,11] this property is exploited by the International Pellet Watch program to monitor the global distribution of persistent organic pollutants.[12,13] The sorption affinity and sorption capacity of plastic particles depends on the nature of the polymeric material, e.g. the degree of crystallinity,[14-16] the extent of weathering/aging of the plastic material[17,18] and the nature thereof (surface-eroding or bulk-eroding),[19-21] as well as the chemical functionality of the polymer backbone and the associated compounds.[22-24] The types of interactions between organic contaminants and polymers include hydrogen bonding between O-containing and/or N-containing functional groups on the polymer and polar moieties on the target organic,[25,26]

π–π, dipole-dipole, electrostatic, and hydrophobic interactions.[27] For example, the high capacity for sorption of the pesticide fipronil by the biodegradable polymers polylactic acid (PLA) and polybutylene succinate (PBS) was ascribed to the high oxygen-containing functional group content of the polymers.[25] Plastic particles can thus be considered as a type of binding phase for pollutants and essential compounds, and chemical speciation analysis of environmental systems must take into account the presence and sink/source functioning of plastic particles. The relative amount and reactivity of contaminants associated with plastic particles in a given setting will be a function of the prevailing conditions, including pH and salinity, as well as the concentrations, affinities and kinetic features of other potential sorbents for the target compound, e.g. natural organic matter (NOM). Indeed, it may well be the case that, depending on the technique used, plastic particles are included to some extent in measured NOM values.

In addition to the effects of plastic particles on the chemical speciation and potential bioavailability of compounds in the exposure medium, their reactivity within organisms is fundamental for understanding and prediction of potential adverse effects. Upon ingestion by biota, the ensuing internal exposure conditions derive from the uptake/release kinetics in the local environment within the organism, and the effective exposure time. For example, laboratory studies have shown that organic pollutants are released more rapidly from MPs in simulated gut media than in seawater.[28] Whilst there is ongoing debate in the literature as to the relevance of so-called trojan horse effects for aquatic organisms under environmentally relevant scenarios,[29,30] there is evidence for its importance for seabirds,[31,32] and indeed the kinetic features of drug release from polymer particles have long been actively exploited to optimise bioavailability in therapeutic contexts.[33,34] In environmental context, the toxicity of plastic leachates – extracted from the plastic material prior to exposure – has been demonstrated.[35,36] Disparate information has been reported from laboratory studies on the effects of contaminants in combination with MPs and nanoplastics (NPs): the body burden and/or toxicity of organic contaminants may be decreased,[37,38] increased,[39,40] or unaffected,[41,42] depending on the spatial and temporal conditions in the exposure medium and within the organism,[43,44] the extent to which the contaminants are released from the particles within the organism (which is generally not determined[45]), and the measured toxicological endpoint. Clarification of the potential risks to aquatic organisms posed by polymer additives and other acquired co-contaminants requires a mechanistic approach that accounts for the dynamic nature of the involved processes including characterisation of the uptake/release kinetics of contaminant-MP/NP interactions, concentration gradients in the polymer and aqueous phases, sorption affinity of the polymer backbone for each (class of) contaminant, particle size, local exposure conditions *within* organisms as well as the particle residence time and location within the organism (gut vs muscle tissue vs lipid-rich tissues etc.).[46,47] Lack of consideration of these factors underlies the disparate reports in the literature.[37-42] Robust assessment of the effect of plastic particles on the chemical speciation, bioavailability and potential toxicity of contaminants requires characterisation of their sink/source functioning under the *local* prevailing conditions. Furthermore, meaningful interpretation of much of the body of literature data is hindered by lack of characterization of the exposure medium. For example, often plastic particles and contaminants are mixed in the exposure medium – sometimes for a specified time period prior to introduction of organisms and sometimes not – without subsequent characterization of the ensuing chemical speciation, i.e. the extent to which the contaminants are associated with the MPs, and the temporal evolution thereof over the exposure duration, is unknown.[48,49] To date the kinetics of the involved processes have generally been treated in a cursory manner, typically involving empirical fitting of data often without explicit accounting for fundamental physicochemical parameters, let alone transient features over the release and accumulation stages.[29,30,50-55]

Herein we elaborate a generic theoretical framework for describing the uptake and release kinetics of organic compound association with plastic particles. The underlying concepts account for the physicochemical features of the target organic compounds and the plastic particles, and is applicable across all organic compounds and plastic polymer types. The developed framework builds on concepts established for dynamic speciation analysis by solid-phase microextraction (SPME),[56-60] and the size-dependent reactivity features of particulate complexants,[46,59-63] and thereby accounts for chemical speciation dynamics within both the aqueous medium and the polymer phase.

Theory

A range of factors contribute to the overall uptake and release kinetics of organic compound association with plastic particles. The passive sampling literature typically assumes that the uptake and release kinetics simply mirror each other.[64] Evidently this is a gross oversimplification that disregards the potential influence of chemical speciation dynamics in both the aqueous medium and in the polymer phase. That is, uptake rates may be limited by the dissociation kinetics of complexed organic species in the aqueous phase,[59,60] and release rates may be limited by the dissociation kinetics of complexes between the organic compound and the polymer backbone.[46] Our generic framework explicitly accounts for all the involved factors, as detailed below.

Diffusion of organic molecules in polymer matrices

When considering the nature of diffusion of organic molecules in polymeric matrices it is important to distinguish between the amorphous, rubbery state which prevails at temperatures above the glass transition temperature, T_g, and the glassy, crystalline state which occurs at $T < T_g$. Segmental mobility of the polymeric chain begins at temperatures above T_g. In practice, ambient environmental conditions correspond to $T > T_g$ for many plastic materials rendering them either completely amorphous, or with amorphous domains. Thus, in most cases of practical interest for micro/nano-plastics in aquatic systems, it is reasonable to assume that diffusion in the polymer phase is Fickian, i.e. transport within the polymer matrix occurs by molecular diffusion satisfying Fick's first and second laws for a single value of the diffusion coefficient.[65] This situation implies that the diffusion rate of the target species is less than the relaxation rate of the polymer chains. The main exception is for unplasticized (glassy) PVC which has a T_g of *ca.* 80 °C:[66] within glassy polymeric phases diffusion can be more complex, i.e. diffusion of molecules can disrupt the structure and diffusion coefficients for organic molecules tend to be much lower than for the amorphous case, and may be concentration dependent because the permeation of compounds effectively plasticises the matrix.[67] Addition of plasticizers lowers the T_g; plasticized PVC typically contains 20-40 w/w % of plasticizers.[68]

For the case of amorphous plastics, the process of diffusion of organic molecules, with size comparable to or larger than the monomer unit of the polymer, involves cooperative movement of several polymer segments when the polymer chain exchanges its position with the diffusing molecule. In this regard the "fractional free volume" concept has found wide application. The approach considers that under given conditions a polymer contains a distribution of free volumes; only those volumes that are large enough to accommodate the target diffusing molecule contribute to the transport.[69] Above T_g the polymer undergoes frequent local conformational transitions that create transient pockets of free volume into which organic molecules can jump.[70] Various empirical models have been developed to predict the diffusion coefficient of organic molecules in polymers and to account for the influence of the size and shape of the diffusing molecule, the effect of temperature, as well as the type of polymer including its degree of crystallinity and the magnitude of the forces between the polymer chains.[71,72] In any case, it is not straightforward to predict the diffusion coefficient of an organic molecule in a polymer phase: in addition to the free volume of the polymer phase, a multitude of other factors are involved including the size and shape of the diffusing molecule.[73,74] The affinity of the target molecule for the polymer backbone must also be properly considered in the determination of experimental data since this determines the fraction which is present in the free (diffusing) form (see below).

Uptake kinetics of organic molecules into plastic particles

Upon immersion of a *pristine* plastic particle (i.e. at $t = 0$ the concentration of X in the particle body, $c_{\mathrm{X,p}} = 0$) into an aqueous solution of a partitioning target organic compound, denoted hereafter as X, a concentration profile develops as a result of diffusion of the analyte into the polymeric phase. During the initial transient stage where t is the primary variable, the concentration of X at the aqueous side of the polymer/water interface, $c^0_{\mathrm{X,w}}$, decreases, and that at the polymer side of the polymer/water interface, $c^0_{\mathrm{X,p}}$, increases. The *transient* flux which dominates at short times is *larger* than the steady-state one.[57] At steady-state, the diffusion layer thickness in the aqueous phase is denoted by δ_{w}, and that in the polymer phase is denoted by δ_{p}. For the case of a spherical particle, $\delta_{\mathrm{p}} = r_{\mathrm{p}}$, whilst for a free-floating planar film δ_{p} corresponds to half the film thickness. The time necessary for establishment of *steady-state transport*, τ_{ss}, corresponds to the highest value of $\delta^2_{\mathrm{p}} / D^{\mathrm{eff}}_{\mathrm{X,p}}$ or $\delta^2_{\mathrm{w}} / D_{\mathrm{w}}$, where $D^{\mathrm{eff}}_{\mathrm{X,p}}$ is the effective diffusion coefficient of X in the polymer phase (see below) and $D_{\mathrm{X,w}}$ is the diffusion coefficient of X in the aqueous phase. The magnitude of $D^{\mathrm{eff}}_{\mathrm{X,p}}$ typically lies in the range 10^{-14} to 10^{-17} m^2 s^{-1}, depending on the nature of X and the polymer type (Table S1); $D_{\mathrm{X,w}}$ is typically of order 10^{-9} to 10^{-10} m^2 s^{-1}, and δ_{w} depends on the hydrodynamic conditions in the medium, with the magnitude in a mildly stirred medium being *ca.* 50 µm.[75] Then $\delta^2_{\mathrm{w}} / D_{\mathrm{X,w}}$ is on the order of 10 s, and for r_{p} between 1 nm and 1 µm, $\delta^2_{\mathrm{p}} / D^{\mathrm{eff}}_{\mathrm{X,p}}$ ranges from 10^{-4} to 10^5 s (*ca.* 28 hr). Accordingly, proper consideration of τ_{ss} is required prior to interpretation of uptake (and release) kinetics of organic molecules into/from plastic particles; at times less than τ_{ss} the kinetics will reflect the relaxation of the transient flux towards its eventual steady-state value.[56,57,76]

Following concepts developed for SPME,[56,58] and assuming first-order kinetics, the temporal evolution of the concentration of X in the polymer phase for times beyond τ_{ss} is given by:

$$\frac{\mathrm{d}\bar{c}_{\mathrm{X,p}}(t)}{\mathrm{d}t} = k_{\mathrm{u}}\bar{c}_{\mathrm{X,w}}(t) - k_{\mathrm{r}}\bar{c}_{\mathrm{X,p}}(t) \qquad (1)$$

where $\bar{c}_{\mathrm{X,p}}(t)$ and $\bar{c}_{\mathrm{X,w}}(t)$ are the average concentrations of X at time t ($t > \tau_{\mathrm{ss}}$) in the polymer and aqueous phases respectively, and k_{u} and k_{r} are the rate constants for uptake and release, respectively. We consider the usual practical case in which $\bar{c}_{\mathrm{X,w}}(t)$ is invariant with time and equal to the concentration in the bulk aqueous phase, $c^*_{\mathrm{X,w}}$, i.e. bulk depletion of the aqueous phase is neglected. Furthermore, we note that $c^*_{\mathrm{X,w}}$ refers to the physicochemical form of X which partitions into the polymeric phase, e.g. some neutral protonated or deprotonated form.[60]

At steady-state, the flux of X, J_{X}, from the aqueous medium into the polymeric particle is given by Fick's first law of diffusion:

$$J_{\mathrm{X}} = \frac{D_{\mathrm{X,w}}(c^*_{\mathrm{X,w}} - c^0_{\mathrm{X,w}})}{(1/\delta_{\mathrm{w}} + 1/r_{\mathrm{p}})^{-1}} = \frac{D^{\mathrm{eff}}_{\mathrm{X,p}}(c^i_{\mathrm{X,p}} - c^0_{\mathrm{X,p}})}{\delta_{\mathrm{p}}} \qquad [\mathrm{mol\ m^{-2}\ s^{-1}}] \qquad (2)$$

where $c^i_{\mathrm{X,p}}$ corresponds to the concentration of X at the geometric center of the polymer phase. The corresponding mass transfer coefficients for diffusive transport in the aqueous phase, m_{w}, and in the polymer phase, m_{p}, are given by:[57]

$$m_{\mathrm{w}} = \frac{D_{\mathrm{X,w}}}{(1/\delta_{\mathrm{w}} + 1/r_{\mathrm{p}})^{-1}} \qquad [\mathrm{m\ s^{-1}}] \qquad (3)$$

$$m_{\mathrm{p}} = \frac{D^{\mathrm{eff}}_{\mathrm{X,p}} K_{\mathrm{pw}}}{\delta_{\mathrm{p}}} \qquad [\mathrm{m\ s^{-1}}] \qquad (4)$$

where K_{pw} is the polymer/water partition coefficient of the target organic compound, equal to $k_{\mathrm{u}}/k_{\mathrm{r}}$. In the steady-state regime, at times well below that for attainment of partitioning equilibrium, τ_{eq}, the temporal evolution of the average concentration of X in the polymer phase corresponds to:

$$\bar{c}_{\mathrm{X,p}}(t) = \frac{A_{\mathrm{p}}}{V_{\mathrm{p}}} J_{\mathrm{X}} t \qquad [\mathrm{mol\ m^{-3}}] \qquad (5)$$

where A_{p} is the surface area of the polymer/water interface and V_{p} is the volume of the polymer phase. For the case of radial diffusion, eq 5 for $t \ll \tau_{\mathrm{eq}}$ can be rewritten as:[77]

$$\bar{c}_{\mathrm{X,p}}(t) = \frac{A_\mathrm{p}}{V_\mathrm{p}}\left(\frac{\delta_\mathrm{w}}{D_{\mathrm{X,w}}} \times \frac{r_\mathrm{p}}{\delta_\mathrm{w} + r_\mathrm{p}} + \frac{1}{m_\mathrm{p}}\right)^{-1} c^*_{\mathrm{X,w}} t \qquad [\mathrm{mol\ m^{-3}}] \qquad (6)$$

from which it follows that:

$$k_\mathrm{u} = \frac{A_\mathrm{p}}{V_\mathrm{p}}\left(\frac{\delta_\mathrm{w}}{D_{\mathrm{X,w}}} \times \frac{r_\mathrm{p}}{\delta_\mathrm{w} + r_\mathrm{p}} + \frac{1}{m_\mathrm{p}}\right)^{-1} \qquad [\mathrm{s^{-1}}] \qquad (7)$$

and

$$k_\mathrm{r} = \frac{A_\mathrm{p}}{V_\mathrm{p} K_\mathrm{pw}}\left(\frac{\delta_\mathrm{w}}{D_{\mathrm{X,w}}} \times \frac{r_\mathrm{p}}{\delta_\mathrm{w} + r_\mathrm{p}} + \frac{1}{m_\mathrm{p}}\right)^{-1} \qquad [\mathrm{s^{-1}}] \qquad (8)$$

From inspection of eqs 7 and 8 it is evident that the rate constants for uptake and release will decrease with increasing r_p, eventually becoming independent of r_p once $r_\mathrm{p} >> \delta_\mathrm{w}$.

As the water/polymer partitioning process progresses, the concentration profiles gradually evolve, and as t approaches t_eq the concentration of X in the polymeric phase approaches its final equilibrium value, $\bar{c}^{\mathrm{eq}}_{\mathrm{X,p}} = K_\mathrm{pw} c^*_{\mathrm{X,w}}$. The evolution of $\bar{c}_{\mathrm{X,p}}$ over the entire accumulation time ($t > \tau_\mathrm{ss}$) is given by:

$$\bar{c}_{\mathrm{X,p}}(t) = K_\mathrm{pw} c^*_{\mathrm{X,w}}[1 - \exp(-k_\mathrm{r} t)] \qquad [\mathrm{mol\ m^{-3}}] \qquad (9)$$

In the case of uptake of X into a polymer phase from a medium containing complexed and free X, in which only the free X is accumulated, the overall flux across the diffusion layer in the aqueous medium towards the polymer/medium interface is governed by the coupled diffusion of the labile species of X. Labile species are those that are capable of maintaining chemical equilibrium with the free form of the target compound X over the various diffusion zones. The expression for k_r becomes:[60]

$$\bar{k}_\mathrm{r} = \frac{A_\mathrm{p} \bar{D}_{\mathrm{X,w}}}{V_\mathrm{p} K_\mathrm{pw} [c^*_{\mathrm{X,w}} / (c^*_{\mathrm{X,w}} + c^*_{\mathrm{X,lab}})] \bar{\delta}_\mathrm{w}} \qquad [\mathrm{s^{-1}}] \qquad (10)$$

where $\bar{k}_\mathrm{r}$ is the effective rate constant for the system containing complexed forms of X in the aqueous medium, $c^*_{\mathrm{X,lab}}$ is the concentration of all labile species of X in the aqueous medium, and $\bar{\delta}_\mathrm{w}$ is the thickness of the joint steady-state diffusion layer in the aqueous medium as derived from the mean diffusion coefficient $\bar{D}_{\mathrm{X,w}}$. Within the diffusive layer there is a concentration gradient of the target organic molecule: when different complexed forms are present, this can lead to changes in the various diffusion rates as a result of the differences in binding strength for the complexing components within the diffusive layer, i.e. the applicable diffusion coefficient and stability constant may both become functions of distance within the diffusive layer.[78] In a medium containing complexed forms of X, for the same given total concentration of X, the coupled diffusion of labile complexed forms of X results in a k_r that is *greater* than that for a solution containing only free X. Consequently the eventual partition equilibrium between the polymeric and aqueous phases is attained faster in the presence of labile complexed forms of X.[59,60] The situation may become more involved when species other than free X partition into the polymer phase,[79] and when the dissociation kinetics of the complexed forms of X are the rate limiting step in the uptake kinetics. Complex dissociation kinetics for a range of chemical species are discussed in detail in our previous work.[59,60,62,63,80]

Release kinetics of organic molecules from plastic particles

Depending on the relative magnitudes of the involved parameters, the release kinetics may be governed by diffusion in the aqueous diffusion layer, diffusion in the polymer phase, or by the dissociation kinetics of complexes between the organic molecule and the polymer backbone.[46] As discussed above, the presence of different complexed forms can lead to changes in the various diffusion rates as a result of the differences in binding strength for the complexing components within the diffusive layer.[78] As detailed in previous work,[63,81] a composite rate constant, k_d, for dissociation of an entity X from a spherical particle is given by:

$$k_d = (1/k_{d,p} + 1/k_d^{is})^{-1} \qquad [s^{-1}] \qquad (11)$$

where $k_{d,p}$, is the diffusion-controlled rate constant:

$$k_{d,p} = 3D_{X,p}^{eff}(1 + K_{int}c_S)/r_p^2 \qquad [s^{-1}] \qquad (12)$$

where K_{int} is the intrinsic stability constant of the inner-sphere complex between the organic molecule and the polymer backbone ($m^3\ mol^{-1}$), and c_S is the concentration of complexing sites in the polymer body ($mol\ m^{-3}$), and k_d^{is} is the rate constant for dissociation of the inner-sphere complex between the organic molecule and the polymer backbone, given by:

$$k_d^{is} = k_a^{is}/K_{int} \qquad [s^{-1}] \qquad (13)$$

where k_a^{is} is the rate constant for formation of the inner-sphere complex between the organic molecule and the polymer backbone ($m^3\ mol^{-1}\ s^{-1}$).

The data collated in Table S1 show that the effective diffusion coefficients, $D_{\mathrm{X,p}}^{\mathrm{eff}}$, for organic molecules in polymer phases are orders of magnitude lower than those for diffusion in bulk aqueous media. Accordingly, we focus herein on the case in which organic molecules are located within the body of the plastic particle and the release kinetics are governed by diffusion within the particle body (i.e. the dissociation kinetics of any inner-sphere complexes with the polymer backbone are immaterial). We follow the rationale previously developed for metal ions,[46] using the mathematical framework developed by Crank.[77] The leading conservation equation for diffusive release of an organic molecule, X, from a spherical body of radius r_{p} into the surrounding aqueous medium is:

$$\frac{\partial c_{\mathrm{X,p}(r,t)}}{\partial t} = D_{\mathrm{X,p}}^{\mathrm{eff}} \left[\frac{\partial^2 c_{\mathrm{X,p}(r,t)}}{\partial r^2} + \frac{2}{r} \left(\frac{\partial c_{\mathrm{X,p}(r,t)}}{\partial r} \right) \right] \qquad (14)$$

where r is the distance from the center of the polymer particle, and $c_{\mathrm{X,p}(r,t)}$ is the concentration of organic species inside the particle at position r and time t, and $D_{\mathrm{X,p}}^{\mathrm{eff}}$ is the effective diffusion coefficient for X inside the particle body. Eq 14 covers the entire timescale of the release process, including the transient regime. Considering the diffusing species to be the free organic molecules, with X being immobile during the time of its association with reactive sites on the polymer backbone, then $D_{\mathrm{X,p}}^{\mathrm{eff}}$ simply corresponds to the diffusion coefficient of the free X, given by:

$$D_{\mathrm{X,p}}^{\mathrm{eff}} = \frac{D_{\mathrm{X,p}}^{\mathrm{f}} c_{\mathrm{X,p}}^{\mathrm{f}}}{c_{\mathrm{X,p}}^{\mathrm{t}}} \qquad [\mathrm{m^2\ s^{-1}}] \qquad (15)$$

where $D_{\mathrm{X,p}}^{\mathrm{f}}$ is the diffusion coefficient for the free organic molecule within the particle body, and $c_{\mathrm{X,p}}^{\mathrm{f}}$ and $c_{\mathrm{X,p}}^{\mathrm{t}}$ are the respective concentrations of the free (mobile) X and the total X within the particle. In this context, free X includes all forms of X that are not associated with the polymer backbone, e.g. protonated and deprotonated forms, complexes with metal ions, etc. The ratio $c_{\mathrm{X,p}}^{\mathrm{f}} / c_{\mathrm{X,p}}^{\mathrm{t}}$ inherently accounts for the intrinsic stability, K_{int}, of the associate between X and the polymer backbone.

Eq 14 is solved under the initial and boundary conditions for the case of (i) randomly distributed X in the particle body at the start of the release process, and (ii) insignificance of the fast diffusion inside the external medium, such that the concentration of X at the medium side of the particle/medium interface is essentially zero. The latter condition requires a sufficiently low volume fraction of plastic particles. Together these conditions correspond to:

initial condition:

$$t = 0: \quad 0 < r < r_\mathrm{p} : c_\mathrm{X} = c_\mathrm{X,p}; \quad r > r_\mathrm{p} : c^*_\mathrm{X,w} = 0 \tag{16a}$$

where $c_\mathrm{X,p}$ is the initial uniform concentration of X inside the particle.

boundary condition:

$$t > 0; \quad r = r_\mathrm{p} : c^0_\mathrm{X,w} = 0 \tag{16b}$$

with $c^0_\mathrm{X,w}(r = r_\mathrm{p})$ being the concentration of X in the aqueous phase at the plastic particle/water interface.

The solution for eq 11 with boundary conditions eq 16a and eq 16b is:[77]

$$\frac{\mathrm{X}(t)}{\mathrm{X}(t \to \infty)} = 1 - \left(\frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left[-n^2 \pi^2 (t/\tau) \right] \right) \tag{17}$$

where X(t) is the *amount* of X that has been released from the spherical particle at time t, $\mathrm{X}(t \to \infty)$ is the amount that has been released at infinite time, and τ is the fundamental time constant (= $r_\mathrm{p}^2 / D^\mathrm{eff}_\mathrm{X,p}$) for diffusive release of X from the particle.

For a thin film plastic entity, the applicable expression is:[77]

$$\frac{\mathrm{X}(t)}{\mathrm{X}(t \to \infty)} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp\left[\frac{-D^\mathrm{eff}_\mathrm{X,p} (2n+1)^2 \pi^2 t}{4(L/2)^2} \right] \tag{18}$$

where L is the film thickness (which is assumed to be much smaller than the other dimensions of the film).

Results and Discussion

Uptake kinetics of organic molecules into plastic particles

The evolution of k_u and k_r as a function of K_pw and particle size, computed using the theoretical framework detailed in the preceding sections, is shown in Figure 1. In accordance with the SPME and passive sampling literature for various polymers, at lower values of K_pw, mass transfer is limited by diffusion inside the polymer phase; at higher values of K_pw, mass transfer is limited by diffusion in the aqueous diffusion layer.[58,82,84] The transition stage where the limiting mass transfer step switches from diffusion in the polymer to diffusion in the aqueous diffusion layer is inversely dependent on $D^\mathrm{eff}_\mathrm{X,p}$ (and is independent of r_p), i.e. the lower is $D^\mathrm{eff}_\mathrm{X,p}$, the higher is the K_pw value at which diffusion in the aqueous diffusion layer is mass transfer limiting. The data in Figure 1 were computed using a $D_{\mathrm{X,p}}^{\mathrm{eff}}$ of 10^{-14} m^2 s^{-1} and $D_{\mathrm{X,w}}$ of 5×10^{-10} m^2 s^{-1}, for which the transition stage is seen to occur at $K_{\mathrm{pw}} \approx 10^5$. For $D_{\mathrm{X,p}}^{\mathrm{eff}}$ of 10^{-12} m^2 s^{-1} the transition occurs at $K_{\mathrm{pw}} = 10^3$, and for $D_{\mathrm{X,p}}^{\mathrm{eff}}$ of 10^{-17} it occurs at $K_{\mathrm{pw}} = 10^8$.

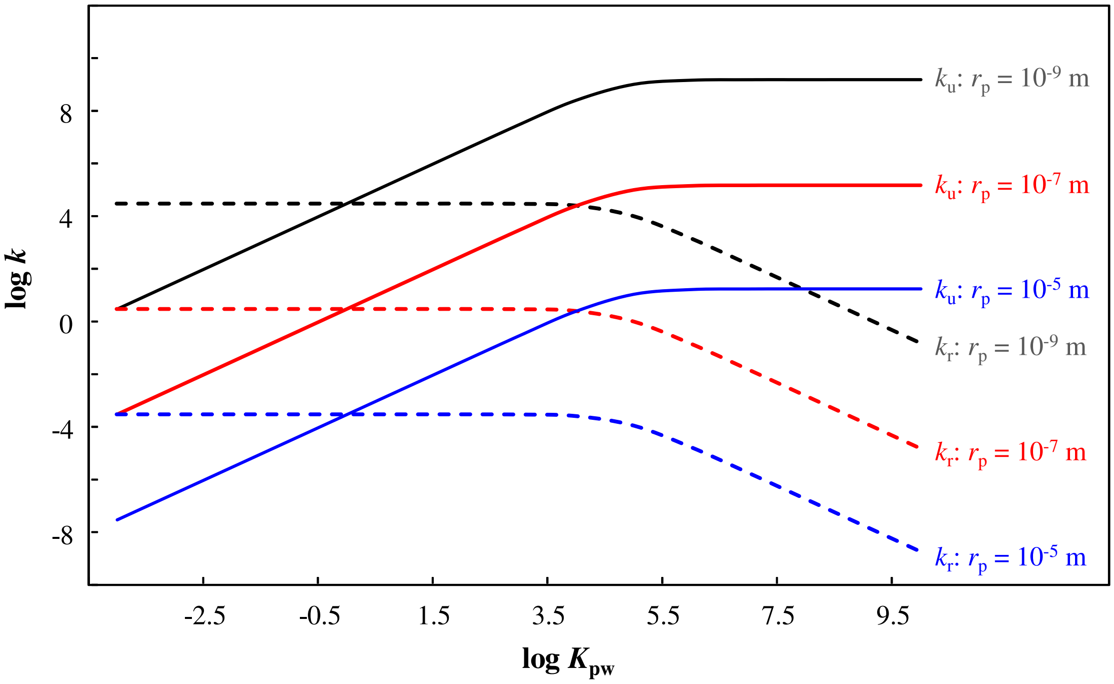

Figure 1. Rate constants for uptake, k_{u} (eq 7), and release, k_{r} (eq 8), of an organic molecule into/from a spherical polymeric particle as a function of the equilibrium partitioning coefficient, K_{pw}, and the particle radius, r_{p}. Computations are performed for $D_{\mathrm{X,p}}^{\mathrm{eff}} = 10^{-14}$ m^2 s^{-1}, $\delta_{\mathrm{p}} = r_{\mathrm{p}}$, $D_{\mathrm{X,w}} = 5\times10^{-10}$ m^2 s^{-1}, and $\delta_{\mathrm{w}} = 5\times10^{-5}$ m.

The temporal evolution of $\bar{c}_{\mathrm{X,p}}$ (eq 9) as a function of r_{p} and K_{pw} is shown in Figure 2 for the case of a non-complexing bulk aqueous medium, $D_{\mathrm{X,w}} = 5\times10^{-10}$ m^2 s^{-1} and $D_{\mathrm{X,p}}^{\mathrm{eff}} = 10^{-14}$ m^2 s^{-1}. Note the enormous increase – *ca.* 10 orders of magnitude – in the timescale of the partitioning process as r_{p} increases from 10 nm (Figure 2B; time to achivement of 95% of the equilibrium concentration of X in the polymer phase is 10^{-2} s for $K_{\mathrm{pw}} = 10^2$ and 0.2 s for $K_{\mathrm{pw}} = 10^6$) to 1 mm (Figure 2C; time to achivement of 95% of the equilibrium concentration of X in the polymer phase is 10^8 s for $K_{\mathrm{pw}} = 10^2$ and 2×10^8 s for $K_{\mathrm{pw}} = 10^6$). As illustrated by the data in Figure 1, when $K_{\mathrm{pw}} = 10^2$ the conditions in Figure 2 correspond to diffusion in the aqueous diffusion layer being mass transfer limiting, whilst when $K_{\mathrm{pw}} = 10^6$ diffusion in the particle body is the mass transfer limiting step. As the particle radius increases, the timescale of the partitioning process for $K_{\mathrm{pw}} = 10^2$ approaches that for $K_{\mathrm{pw}} = 10^6$, in line with the known features of particle reactivity, i.e. the diffusive supply flux from the aqueous medium decreases as r_{p} increases.[63,85] The effect of r_{p}, $D_{\mathrm{X,p}}^{\mathrm{eff}}$, and K_{pw} on the temporal achievement of 95% of the equilibrium concentration of X in the polymer phase is shown in Figure 3. The transition between K_{pw}-independent and K_{pw}-dependent values corresponds to the transition between mass transport being limited by diffusion in the polymer matrix versus diffusion in the bulk aqueous medium, respectively (*cf.* Figure 1).

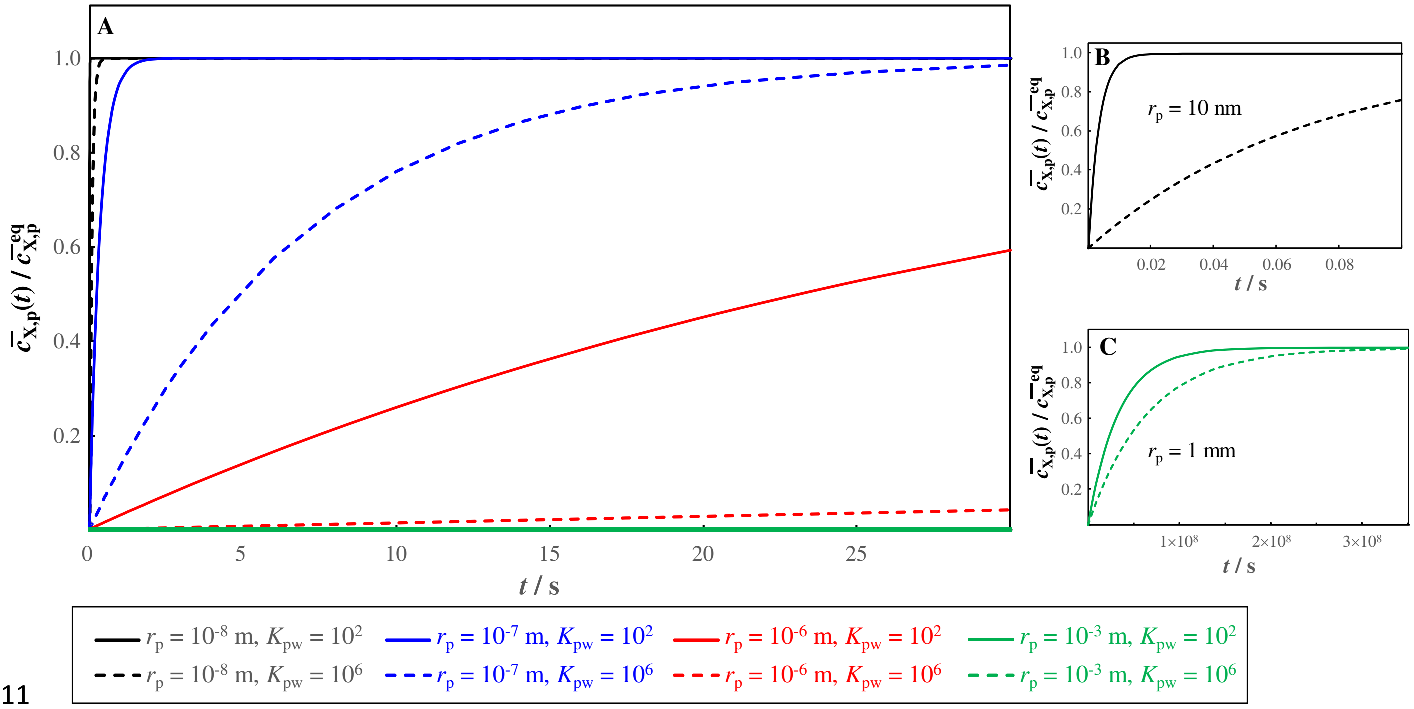

Figure 2. Temporal evolution of the average concentration of X in the polymer phase as a function of the spherical particle radius, r_{p}, and the polymer/water partition coefficient, K_{pw}. **A**: Data are shown for $r_{\mathrm{p}} = 10^{-8}$ m (black curves), 10^{-7} m (blue curves), 10^{-6} m (red curves), and 10^{-3} m (green curves), and K_{pw} values of 10^{2} (solid curves) and 10^{6} (dashed curves). **B**: Amplification of the data for $r_{\mathrm{p}} = 10^{-8}$ m. **C**: Amplification of the data for $r_{\mathrm{p}} = 10^{-3}$ m. $D_{\mathrm{X,p}}^{\mathrm{eff}} = 10^{-14}$ m^{2} s^{-1} in all cases.

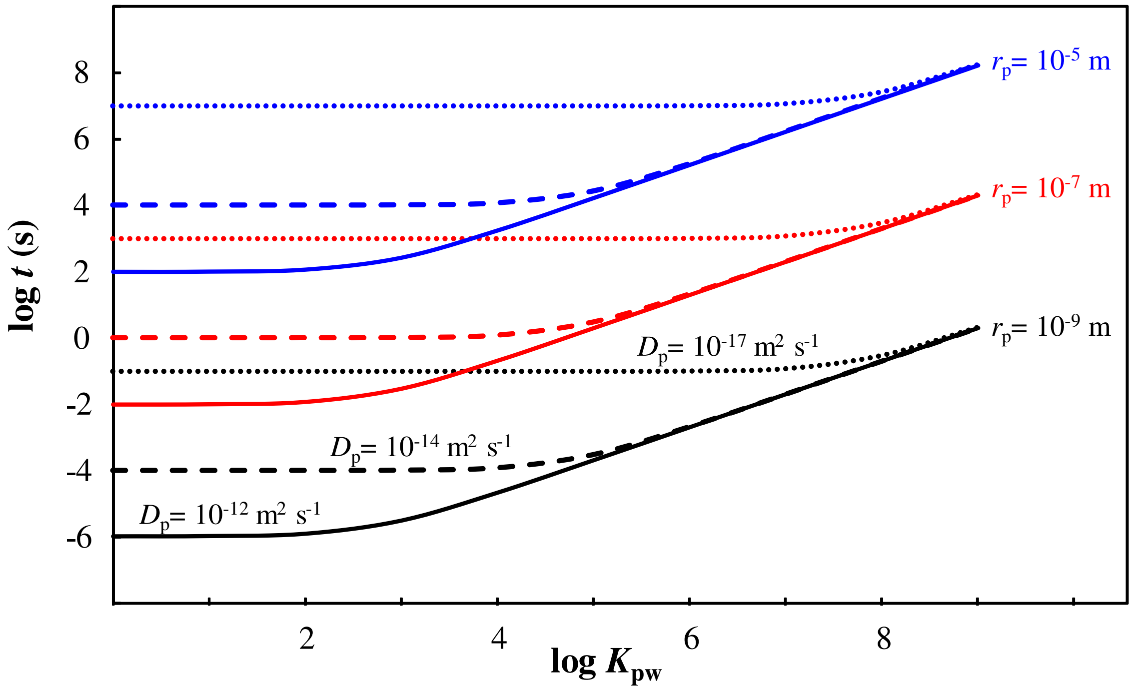

Figure 3. The effect of the partitioning coefficient, K_{pw}, on the temporal achievement of 95% of the equilibrium concentration of X in the polymer phase immersed in a non-complexing bulk aqueous medium. Data are computed for spherical particles with radius $r_{\mathrm{p}} = 10^{-9}$ m (black curves), 10^{-7} m (red curves), and 10^{-5} m (blue curves), and $D_{\mathrm{X,p}}^{\mathrm{eff}}$ values of 10^{-12} m^2 s^{-1} (solid curves), 10^{-14} m^2 s^{-1} (dashed curves), and 10^{-17} m^2 s^{-1} (dotted curves). In all cases $D_{\mathrm{X,w}} = 5\times10^{-10}$ m^2 s^{-1}, $\delta_{\mathrm{w}} = 5\times10^{-5}$ m, and $\delta_{\mathrm{p}} = r_{\mathrm{p}}$.

The theoretical framework presented herein can be applied to obtain more rigorous understanding of the growing body of literature reports on the observed uptake kinetics of organic compounds by plastic particles. Such uptake curves are typically described by empirical fitting, without explicit assessment of the mass transfer-limiting step nor consideration of the transient regime.[17,18,51,54,55,86] As an illustrative example, we consider data reported for sorption of pyrene by polyethylene microparticles (r_{p} in the range 50 to 75 µm, $T = 25$ °C), for which the authors stated that the diffusive supply flux in the aqueous medium could not be the rate-limiting step in the uptake process because the solution was agitated during the sorption process.[86] Such reasoning is too simplistic: as detailed above, the step which is mass transfer limiting is determined by the relative magnitude of k_{u} and k_{r} and thus the relevant polymer/water partition coefficient, diffusion coefficients in the aqueous and polymer phases, the particle size, and the thickness of the diffusion layer in the polymer phase and in the aqueous medium. Rigorous analysis of the data in terms of the conceptual framework presented herein, together with the experimentally observed K_{pw} of $10^{3.2}$,[86] independently determined values of $D_{\mathrm{X,p}}^{\mathrm{eff}}$ (5.47×10^{-14} m^2 s^{-1} at 24 °C [87]), and $D_{\mathrm{X,w}}$ ($9.2\mathrm{x}10^{-10}$ m^2 s^{-1} at 25

°C [88]), and a δ_w of 5×10^{-5} m applicable for a continuously agitated system,[75] provides a sound basis for establishing that diffusion in the particle body is the mass transfer limiting step in the uptake process. Indeed the experimental data are in gratifyingly good agreement with the theoretical curves for this case (Figure 4, black curves).

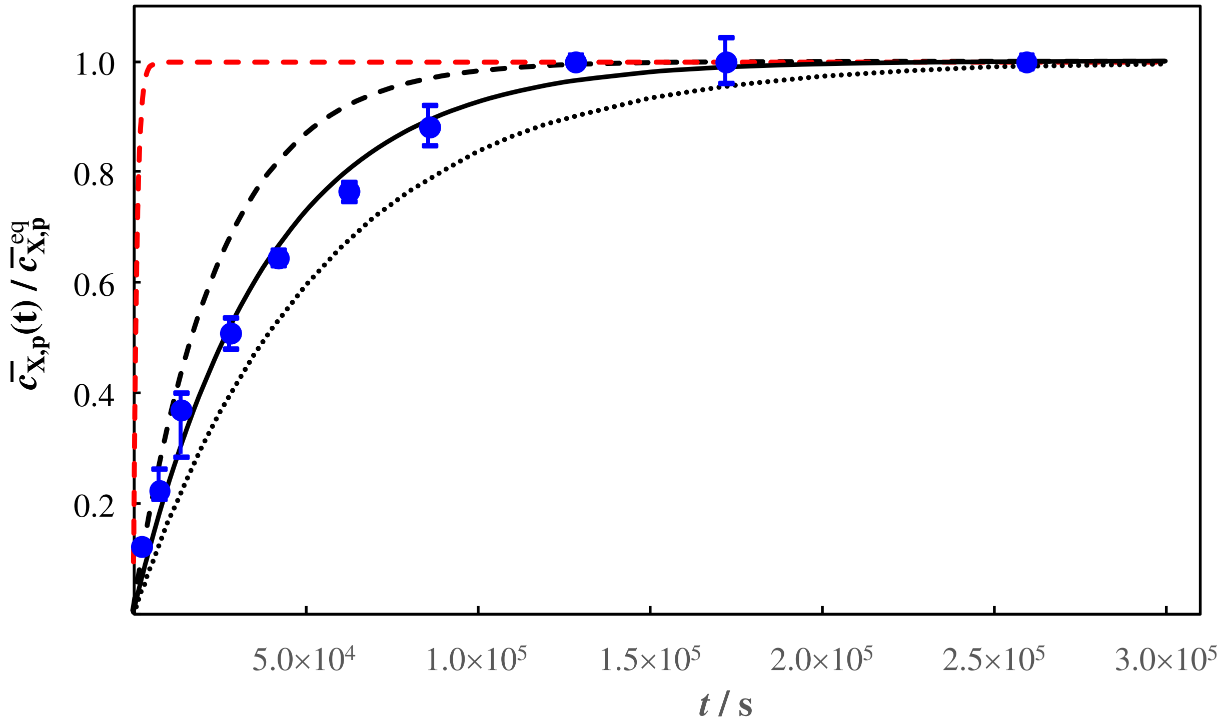

Figure 4. Temporal evolution of pyrene uptake by polyethylene microparticles. Experimental data (solid blue circles and corresponding error bars) were measured for particles in the size range r_p = 50 – 75 µm; for some data points the reported error bars were smaller than the symbol size.[86] The theoretical curves for mass transfer being limited by diffusion in the polymer body were computed using eq 9 with $r_p = 5\times10^{-5}$ m (dashed black line), 6.25×10^{-5} m (solid black line), or 7.5×10^{-5} m (dotted black line), together with $D_{X,p}^{eff} = 5.47\times10^{-14}$ m^2 s^{-1},[87] $D_{X,w}$ = 9.2×10^{-10} m^2 s^{-1},[88] and $\delta_w = 5\times10^{-5}$ m. The theoretical curve for mass transfer being limited by diffusion in the aqueous diffusion layer (red line) was computed using eq 9 with $r_p = 6.25\times10^{-5}$ m, $D_{X,w} = 9.2\times10^{-10}$ m^2 s^{-1}, [88] δ_w = 5×10^{-5} m, and $D_{X,p}^{eff}$ set equal to $10\times D_{X,w}$.[77]

Release kinetics in aqueous media

Theoretical curves for the release kinetics of compounds from plastic particles showing the effect of particle size, diffusion coefficient of X in the polymer, and the affinity of X for the polymer backbone, were presented in our previous work (for X = a metal ion).[46] There is a large body of literature reports on the observed kinetics of release of organic compounds from plastic particles into various aquatic media. Similar to the case of uptake discussed above, description of the experimental data is typically limited to empirical curve fitting.[18,24,55,89] When diffusion within the particle body governs the release kinetics of a compound X from a spherical particle, the temporal evolution of the amount of X released from the particle can be described by eq 17, where the applicable boundary conditions (eqs 16a and 16b) correspond to a particle initially loaded with X being immersed in a medium where the concentration of X is zero at $t = 0$. The smaller the particle size, and the greater the diffusion coefficient, the faster will be the release kinetics (because the fundamental time constant for the process corresponds to $r_{\mathrm{p}}^2 / D_{\mathrm{X,p}}^{\mathrm{eff}}$; see Theory Section and ToC graphic). Figure 5 shows that experimental data corresponding to the boundary conditions of eq 17, specifically immersion of phenanthrene-loaded polyethylene microparticles in simulated gut conditions,[28] are well described by eq 17, using a $D_{\mathrm{X,p}}^{\mathrm{eff}}$ value of 1.7×10^{-13} $\mathrm{m}^2\ \mathrm{s}^{-1}$ for the applicable T of 38 °C in line with independently determined values at $T = 20$ °C (7.5×10^{-14} $\mathrm{m}^2\ \mathrm{s}^{-1}$ [90]; 1.86×10^{-13} $\mathrm{m}^2\ \mathrm{s}^{-1}$ [91]; 3.55×10^{-13} $\mathrm{m}^2\ \mathrm{s}^{-1}$ [92]). The slight deviation between the computed and experimental data seen at short times in Figure 5 may reflect the presence of some smaller particles, or inhomogeneity in the concentration profile of phenanthrene within the particle body (the sorption time prior to the release studies was not specified,[28] and computations indicate that a time frame of the order of 100 h would be required to achieve 95% of the equilibrium concentration of phenanthrene in the polyethylene phase (for $K_{\mathrm{pw}} \approx 10^4$) [91-94]).

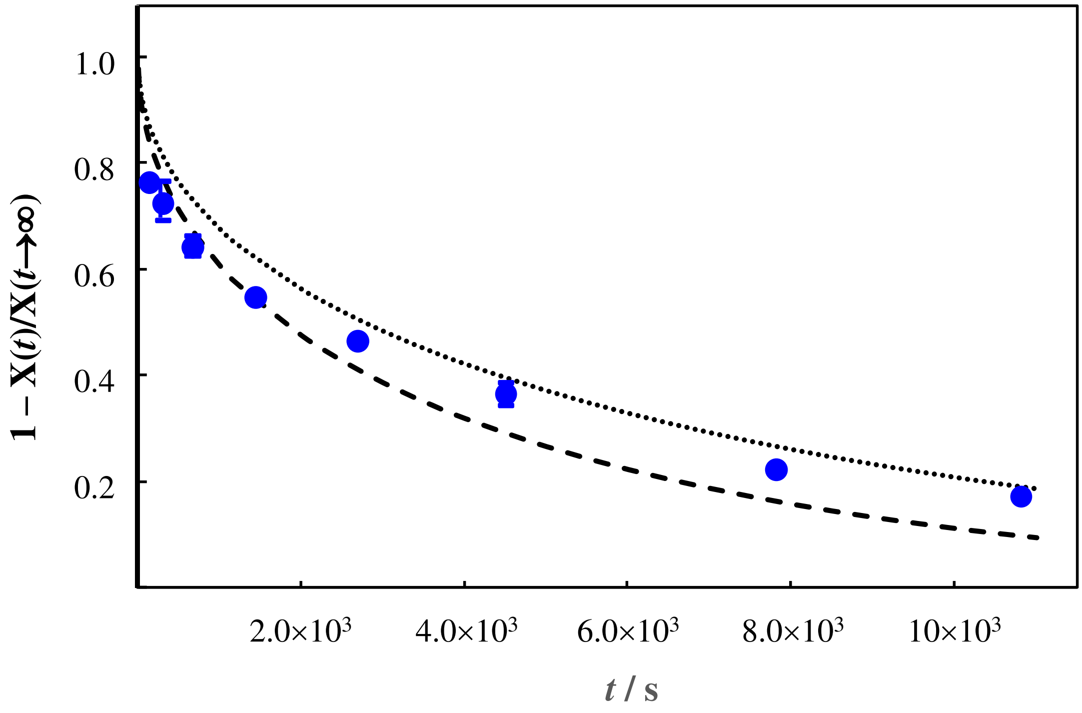

Figure 5. Time evolution of release of phenanthrene from polyethylene microparticles. Experimental data (solid blue circles and corresponding error bars) were measured for phenanthrene-loaded polyethylene microparticles (r_p = 100 – 125 μm) immersed in simulated gut media (15 mM sodium taurocholate in seawater at pH 4, T = 38 °C); for most data points the reported error bars were smaller than the symbol size.[28] The theoretical curves were computed using eq 17 with $D_{\mathrm{X,p}}^{\mathrm{eff}}$ = 1.7×10^{-13} $\mathrm{m^2\ s^{-1}}$ and r_p = 100 μm (dashed black line) or 125 μm (dotted black line).

Release kinetics in biota

Much of the literature on the effect of micro- and nano- plastics on biouptake and/or effects of particle-associated organic pollutants on organisms is poorly defined and/or insufficiently documented to enable quantitative interpretation. For example, often the chemical speciation in the exposure medium is not characterised and thus the extent to which the organic pollutants are associated with the plastic particles are unknown. Also, in many cases it is not evident whether the eventual body burden of organic pollutants corresponds to that which has been released from ingested plastic particles, or rather represents the sum of the released and remaining particle-bound compounds.[95,96] Furthermore, models which ignore the role of particle size in predicting the potential for organic compounds associated with plastic particles to be transferred to biota are bound to yield physicochemically poor outcomes.[29,30] For example, application of eq 17 shows that on the timescale of 1 h, compounds with $D_{\mathrm{X,p}}^{\mathrm{eff}}$ of 10^{-16} $\mathrm{m^2\ s^{-1}}$ (at the lower end of the range of reported values, Table S1) would be completely released from particles with radii of 100 nm or smaller, whilst negligible release would occur in 1 h from particles with radii on the order of 100 μm or greater (see also the ToC graphic).

One recent experimental study[97] has reported sufficient information to enable us to make a semi-quantitative interpretation. Specifically, mussels (*Mytilus galloprovincialis*) were exposed to the same total concentration of benzo(a)pyrene (BaP) in the freely dissolved form and sorbed in polyethylene microparticles (r_p = 10 to 12.5 μm): after 7 days, the amount of BaP accumulated in the digestive gland was approximately the same for the water-borne and plastic-associated exposures.[97] These results can be explained by the observation that mussels eliminate ingested microplastic particles with dimensions of the order of 10 μm within a few hours,[98] and that complete desorption of BaP from the polyethylene microplastics is predicted to occur within *ca.* 1 h (estimated using eq 17 with $r_\mathrm{p} = 10\ \mu\mathrm{m}$ and $D_\mathrm{X,p}^\mathrm{eff} = 10^{-14}\ \mathrm{m}^2\ \mathrm{s}^{-1}$ [87,92]). Thus, in this example the microplastic associated BaP in the exposure medium is fully bioavailable and hence fully labile on the timescale of bioaccumulation by the organism. In the general context of bioavailability in aquatic environments and risk assessment, it is necessary to account for the amount of contaminants associated with plastics *and* their uptake/release kinetics (as deriving from the particle size and $D_\mathrm{X,p}^\mathrm{eff}$ values) relative to those of other ingested particles such as food and sediment.

The modelling framework elaborated herein provides order-of-magnitude estimates of the characteristic times for uptake and release of organic molecules from plastic particles, which may serve as an important starting point for future work. We have considered the most straightforward case in which the physicochemical features of the plastic particles (size, porosity, chemical functionality, etc.) and the diffusion coefficient of the target compound is invariant with time. In addition to the environmental aspects detailed herein, the conceptual framework is applicable in a range of contexts including e.g. design of dosing systems for toxicity testing of poorly soluble compounds.[99,100] Our findings highlight the crucial role of the size of the plastic particle in determining the uptake/release kinetics of associated molecules. This fundamental aspect is currently ignored in the context of developing standard test procedures for assessing migration of contaminants in plastics, e.g. with regard to human exposure via food packaging or toys.[101-104]

Development of a more sophisticated interpretation framework is hindered by the current lack of quantitative information on the pore structure within the particle body, the thermodynamic and kinetic features of the immobile X-polymer species, and the homogeneity of the particle body in terms of e.g. the degree of crystallinity. Environmental risk assessment of plastic particles also requires knowledge on how these properties evolve as a function of physical and chemical degradation of the polymeric structure.[105] In this regard, the behaviour of new bio-based, biodegradable polymers is of interest: the purported faster degradation kinetics of these materials has consequences for the speciation and fate of associated polymer additives and other organic contaminants. Future work will extend the framework to account for the effects of the timescale and extent of ageing/weathering of the plastic particles on the uptake/release kinetics of associated compounds.

Supporting Information

Table of collated literature data on measured effective diffusion coefficients in various types of polymer phases and polymer-water partition coefficients for a range of organic compounds including typical polymer additives and environmental contaminants (PDF)

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