Sorption of Hydrophobic Organic Compounds to Plastics in the Marine Environment: Equilibrium

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Abstract Marine plastics have shown to contain various environmental chemicals. For evaluating the potential of plastics to influence regional and global dynamics of these chemicals and to serve as a vector to marine biota, understanding of sorption and desorption of chemicals by plastics is important. In this chapter, the equilibrium sorption of neutral organic chemicals from water to plastics is discussed. First, the basic principles of equilibrium sorption are explained, and then, factors that influence the magnitude of the sorption coefficient, such as types of plastics and chemicals, temperature, coexisting organic and inorganic constituents in water, are overviewed. Successively, effects on the equilibrium sorption properties of field-relevant mechanisms such as degradation and biofouling as well as nano-sized plastics are discussed. It is evident that studies on sorption properties of aged plastics in field conditions are far less available than those of intact plastics in laboratory conditions.

Keywords Degradation, Intermolecular interaction, Marine plastic, Nanoplastic, Sorption coefficient

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Contents

1 Introduction

Plastic particles and fragments existing in marine environments have been found to contain various types of chemicals. Some chemicals are additives that are intentionally compounded into plastic during manufacturing processes, while others are environmental contaminants sorbed by plastic from external phases (e.g., seawater). The ability of plastic to sorb and concentrate hydrophobic organic contaminants (HOCs) from ambient seawater has been recognized since the early 1970s [1, 2] and has received growing interest afterwards [3–11]. Subsequent research has addressed the composition of the chemical mixtures that reside in the plastic particles (e.g., [3, 4, 8]), the global distribution of plastic-bound chemicals by using the plastic as continuous in situ passive samplers [6], the relative ability of various plastic types to sorb chemicals [9, 12, 13], and several more specific mechanistic issues such as the role of plastic as a transport medium [3, 14, 15]. Chemicals in marine plastics can desorb to seawater when the conditions allow them to do so. Moreover, if plastics are ingested by organisms such as birds, fish, and benthic organisms, chemicals could desorb from the plastics within the gastrointestinal tract and become available for successive uptake into the organism body [7, 16–18]. Clearly, understanding of the sorption and desorption behavior of chemicals to and from plastics is of utmost importance for the evaluation of plastic–chemical interactions in marine environments as well as a possible transfer of chemicals from plastics to organisms.

The aim of this chapter is to provide fundamental and practical knowledge regarding equilibrium sorption of organic chemicals from water to plastic. Kinetics of sorption (and desorption) of organic chemicals by plastics are out of scope within this chapter and will be dealt with in another chapter of this book. The first half of this chapter summarizes the principles of equilibrium sorption of organic chemicals to plastics. The concepts of equilibrium sorption and sorption coefficients are introduced, and the relation of sorption coefficients with the properties of plastics and chemicals is described. In the latter half of this chapter, we collate and synthesize the recent research in relation to sorption of organic chemicals by marine plastics. Influences of weathering and biofouling on sorption coefficients and field-based values are overviewed.

2 Principles of Sorption to Polymers

2.1 Sorption: Types and Definitions

Sorption is a process in which chemicals are transferred from a fluid phase (e.g., water and air) to a solid phase. The term "sorption" collectively refers to both absorption and adsorption. In absorption, molecules of the chemical penetrate and become associated within the matrix of the solid phase, while in adsorption, molecules become confined at the interface between fluid and solid phases. The term sorption is widely used, because it is often unknown whether absorption or adsorption is operative, and also because absorption and adsorption can simultaneously occur. The relative importance of absorption and adsorption depends on the properties of the solid and the chemical and on the surface-to-volume ratio of the solid. Plastics have a variety of properties and dimensions, and thus both absorption and adsorption can be relevant. A term that is closely related to sorption is "partitioning." "Partitioning" is more general, referring to a transfer of chemical between any types of phases, in contrast to "sorption," which usually involves a solid as one phase. This word usage is, however, not universal. In fact, "sorption" and "partitioning" are often used as synonyms, and in some scientific fields such as environmental chemistry, "partitioning" is used only to refer to a chemical transfer "into" liquid and solid phases (i.e., absorption) (e.g., [19, 20]).

Sorption processes can also be classified into chemical and physical sorption. Chemical sorption (also referred to as chemisorption) denotes the association of chemicals by solid through the formation of covalent bonds. Thus, for chemisorption to occur, there need to be structural domains in solid and chemical molecules that can mutually react. Chemisorption can be irreversible, i.e., the sorbed chemical will not desorb from the solid to the surrounding phase (unless the covalent bond that connects the chemical and the plastic breaks up). Physical sorption (or physisorption) takes place due to non-covalent intermolecular interactions such as van der Waals (vdW) interactions. Non-covalent interactions occur between any solid and any chemical (though the interaction forces strongly depend on their combinations) and physisorption is usually reversible. Usually, sorption of HOCs by typical marine plastics is physisorption. Therefore, in the following sections of this chapter, we only deal with physisorption.

2.2 Equilibrium Sorption and Sorption Coefficients

In a closed system consisting of a solid phase and a fluid phase (e.g., plastic and water), transfer of a chemical occurs from one phase to the other until the concentrations of the chemical in the two phases become "balanced." The final state, in which there is no net transfer of the chemical between the two phases, is referred to as sorption equilibrium. The concentration ratio at sorption equilibrium is referred to as the sorption coefficient and is typically denoted with K. For sorption by plastics,

$$K_{\mathrm{pw}} = {C_{\mathrm{p}}}^{*}/{C_{\mathrm{w}}}^{*} \tag{1}$$

where K_{pw} [$\mathrm{L_{water}/kg_{plastic}}$] is the sorption coefficient of the chemical from water to plastic and C_{p} [$\mathrm{mol/kg_{plastic}}$ or $\mathrm{mg/kg_{plastic}}$] and C_{w} [$\mathrm{mol/L_{water}}$ or $\mathrm{mg/L_{water}}$] are the concentrations of the chemical in plastic and water, respectively. The superscript * indicates that the two concentrations are in equilibrium. The unit of K_{pw} depends on the units of the two concentrations; thus, if C_{p} was defined with a unit of $\mathrm{mol/L_{plastic}}$ instead, then K_{pw} would be in $\mathrm{L_{water}/L_{plastic}}$. K_{pw} defines the balanced state of C_{p} and C_{w} and the value of K_{pw} depends strongly on the types of plastics and chemicals. For example, a measured value of K_{pw} for PCB 143 (a congener of polychlorinated biphenyls, PCBs) between polyethylene (PE) and water is 6.3×10^{6} $\mathrm{L_{water}/kg_{PE}}$ [21], whereas that of lindane is 4.2×10^{2} $\mathrm{L_{water}/kg_{PE}}$ [22]. This means that, at equilibrium, there is a factor of as much as 10,000 difference between PCB 143 and lindane in terms of the enrichment factor from water.

The sorption coefficient K_{pw} is of tremendous importance for understanding the sorption/desorption behavior of a chemical to plastics, as the spontaneous transfer of a chemical always occurs in such a direction that the actual concentration ratio ($C_{\mathrm{p}}/C_{\mathrm{w}}$) approaches the value of K_{pw}. If the actual $C_{\mathrm{p}}/C_{\mathrm{w}}$ ratio is $<K_{\mathrm{pw}}$, then sorption from water to the plastic occurs. If $C_{\mathrm{p}}/C_{\mathrm{w}} > K_{\mathrm{pw}}$, then desorption from the plastic to water takes place. When $C_{\mathrm{p}}/C_{\mathrm{w}}$ reaches K_{pw}, then neither sorption nor desorption occurs any more (i.e., sorption equilibrium). Equilibrium (or near-equilibrium) situations can occur not only in closed systems, but also in any system where the phase transfer occurs much quicker than other disturbing processes (e.g., degradation of the chemical). For example, sorption of legacy pollutants such as PCBs from seawater to floating plastic particles in the open ocean may proceed until equilibrium is reached, because the seawater concentration of such chemicals is relatively stable over long time. In contrast, sorption of wastewater contaminants to plastics in estuarine systems may not reach equilibrium, as concentrations in the water phase fluctuate steadily.

If K_{pw} is constant through the whole concentration range of the chemical, the sorption is called "linear sorption," because the plot of $C_{\mathrm{p}}{}^{*}$ against $C_{\mathrm{w}}{}^{*}$ is linear. Such a plot is called a linear isotherm, and the slope of the plot equals K_{pw}. Thus,

$$C_{\mathrm{p}}{}^{*} = K_{\mathrm{pw}} C_{\mathrm{w}}{}^{*} \tag{2}$$

In case K_{pw} depends on the concentration of the chemical, the isotherm (i.e., $C_{\mathrm{p}}{}^{*}$–$C_{\mathrm{w}}{}^{*}$ plot) is nonlinear, and the sorption is called "nonlinear." Nonlinear isotherms of plastic sorption can sometimes be approximated by the following Freundlich equation:

$$C_{\mathrm{p}}{}^{*} = K_{\mathrm{Fr}} \left(C_{\mathrm{w}}{}^{*}\right)^{n} \tag{3}$$

where K_{Fr} and n are the Freundlich coefficient and exponent, respectively. If the isotherm follows the Freundlich equation, K_{pw} is equal to $K_{\mathrm{Fr}}\ (C_{\mathrm{w}})^{n-1}$, which shows how K_{pw} depends on the concentration and that K_{pw} is equal to K_{Fr} for C_{w} equal to unity. Many other models exist (e.g., Langmuir, Polanyi, dual-mode [23]) to describe nonlinear isotherms. Concentration-dependence of K_{pw} can be a relevant issue for marine plastics, because lab-experiments are often conducted with concentrations that are much higher than the environmentally relevant range.

Regarding equilibrium sorption, two additional notes may be worth mentioning. First, a high or low K_{pw} value by itself implies neither fast nor slow sorption. Moreover, K_{pw} itself does not infer at all whether or not the actual situation is in equilibrium or the sorption process of concern will ever reach equilibrium in the real world. What K_{pw} implies, in combination with the actual $C_{\mathrm{p}}/C_{\mathrm{w}}$ ratio, is the direction of the phase transfer (either sorption or desorption), as explained above. How sorption/desorption reaches equilibrium is an issue of sorption kinetics. Second, we only discuss neutral chemicals here with a focus on HOCs. Sorption and partitioning of ionic and ionizable chemicals need more considerations than presented in this chapter (see, for example, Chap. 8 of [24]). Many pharmaceuticals, surfactants, and biocides are ionic or ionizable chemicals, for example.

2.3 *What Determines the Sorption Coefficient from Water to Plastic?*

2.3.1 Intermolecular Interactions

K_{pw} strongly depends on the combinations of chemical and plastic. A major determining factor for K_{pw} is the intermolecular interactions that the chemical undergoes in (or on) the plastic phase and in the water phase. If the energy due to the chemical–plastic interactions is more favorable than that of the chemical–water phase interactions, then a higher concentration of the chemical will be found in plastic than in water at equilibrium, i.e., $K_{\mathrm{pw}} > 1$ (assuming absorption mechanisms and full accessibility in plastic). This means that the chemical will be enriched in the plastic phase in comparison to the water phase. HOCs generally show $K_{pw} > 1$ in plastics, and often K_{pw} is many orders of magnitude higher than 1 because of the favorable interaction energies of HOCs residing in plastics in reference to those in water.

The most relevant types of interactions for sorption of neutral organic chemicals are vdW interactions, hydrogen (H)-bonding interactions, and cavity formation [25], and these types of molecular interactions additively contribute to the overall interaction energy of the chemical in a given phase. The former two types of interactions are attractive; thus, stronger interactions lead to a higher affinity of the chemical for the phase of concern. vdW interactions occur between any types of molecules, whereas H-bond interactions occur only between H-bond donor and acceptor molecules. For example, nonpolar polyethylene molecules exert only vdW interactions to any chemical, whereas the water molecule (an H-bond donor and acceptor molecule) undergoes H-bond interactions with many polar chemicals in addition to the universally present vdW interactions. The cavity formation is the (hypothetical) process to create a cavity in the phase to accommodate the molecule to be sorbed. Creation of a cavity needs disruption of mutual interactions between phase-constituting molecules and thus costs energy. Therefore, the larger the cavity formation energy, the smaller the affinity for the phase. The cavity formation energy in the water phase is large and much larger than that in the plastic phase, because of the strong cohesive energy between water molecules. In a given phase, the larger the molecule to be sorbed, the larger the cavity formation cost, because the size of the cavity depends on the size of the coming molecule.

Note that what is important for the sorption coefficient is the “difference” between the molecular interaction energies that occur in plastic and in water, and not the absolute interaction energy in either of the phases. In the literature, it is often incorrectly stated that a high log K_{pw} value is an indication of strong interactions between chemical and plastic. However, a high log K_{pw} value can occur with a relatively low chemical–plastic interaction energy as well, if the chemical–water interaction energy is even lower (e.g., due to a high cavity formation energy cost in water). Similarly, strong chemical–plastic interactions do not necessarily mean that log K_{pw} is high, because they can be compensated by similarly strong or even stronger interactions in the water phase (this is often the reason for relatively low K_{pw} of polar chemicals sorbing from water to nonpolar plastics). For molecular interactions and quantitative predictions of log K_{pw}, also see Sect. 3.5 below.

2.3.2 Phase Properties of Plastics

If we were dealing with the partitioning of chemicals from water into organic solvent, the molecular interactions discussed just above would be more or less the entire story for describing partition coefficients. However, in contrast to a liquid phase where the dissolved chemical can freely move, the matrix of plastics is not necessarily fully accessible for the sorbed chemicals. Marine plastics are synthetic

Table 1 Glass transition temperatures (T_g) of selected synthetic polymers

Plastics	T_g (°C)
Low density polyethylene (LDPE)	−125
Atactic-polypropylene (a-PP)	−20
Isotactic polypropylene (i-PP)	100
Polystyrene (PS)	100
Poly(vinyl chloride) (PVC)	81
Poly(vinyl acetate) (PVA)	28
Poly(dimethylsiloxane) (PDMS)	−123
Poly(ethylene terephthalate) (PET)	69
Polyoxymethylene	−93 to −8[a]

Data are from Carraher [26] unless otherwise noted

[a] Suzuki et al. [28]

organic polymers, and they usually contain crystalline and amorphous regions [26]. A crystalline region has an ordered structure where polymeric molecules are regularly arranged. The atoms consisting of polymer molecules are restricted in terms of the positions and motions. Disrupting tightly associated polymeric chains needs a high energy, and thus chemicals do not favorably absorb to crystalline regions. In an amorphous region, polymeric chains are more randomly oriented, molecular segments have a higher freedom to move, and a larger free volume is available for chemicals to be absorbed. Semi-crystalline polymers, which contain both crystalline and amorphous regions to an appreciable extent and include many commercial polymers such as PE and PP, can absorb the chemicals in their amorphous regions. Indeed, it was reported that the sorption coefficient from water to PE ($K_{PE/w}$) decreases with increasing crystallinity of PE [27]. The degree of crystallinity varies considerably even across polymers with the same repeating structure, as the chain branching and the processing during the polymer productions have strong influences on the formation of crystalline regions [26].

Another important factor is the glass transition. Amorphous regions of the polymer undergo a transition from a rubbery to a glassy state upon cooling below the glass transition temperature (T_g). Polymer molecules in a rubbery state are capable of segmental chain movements, whereas those in a glassy state are restricted to vibrational and short-range rotational motions. Polymers whose T_g is below ambient temperature are called rubbery polymers (e.g., PE; see Table 1), while those with T_g above ambient temperature are called glassy polymers (e.g., poly(vinylchloride) (PVC) and polystyrene (PS)). Various properties including sorption properties of a polymer differ dramatically when compared at temperature below and above T_g. Rubbery regions absorb chemicals as organic solvent dissolves them, because of the relatively high flexibility of the polymer segments. The sorption to a rubbery polymer is usually linear, non-competitive in multi-solute systems, and fully reversible. In contrast, chemicals are said to partition into characteristic nano-sized pores within glassy polymers, and this type of sorption is rather an adsorption-like or pore-filling process [29, 30]. As a result, the sorption of organic chemicals to glassy polymers shows nonlinear isotherms, competition with other coexisting chemicals, and hysteresis due to deformation of the pores [30–32].

2.4 *Influences of External Conditions on the Sorption Coefficient*

Temperature can have influences on plastic–water sorption coefficients in two ways. First, temperature can influence the bulk properties of the polymer such as crystallinity and glassiness and thereby change K_{pw}. A higher temperature generally leads to lower crystallinity and glassiness because the higher energy allows larger motions of polymer segments. Second, the intermolecular interaction energy also depends on the temperature. The data for low density polyethylene (LDPE)–water partition coefficients of PAHs and PCBs show a minor but significant temperature-dependence; an increase by 10°C causes a decrease of K_{pw} by a factor of 1.1–2 [21, 33]. This is comparable to typical solvent–water partition coefficients for HOCs which decrease by a factor of <2 (i.e., <0.3 log units) with an increase of 10°C [24].

Composition of the water phase can have an influence on apparent sorption coefficients. Particularly relevant for hydrophobic chemicals are particulate (POM) and dissolved organic matter (DOM) present in seawater. POM and DOM can significantly sorb chemicals and thereby decrease the sorption of chemicals to plastics. Here, we consider POM and DOM as additional sorbing phases in water and do not consider their potential influences on the sorption properties of plastic and water themselves (see Sects. 3.2 and 3.3 for the latter mechanism). The apparent sorption coefficient from the water phase (including POM and DOM) to plastic (K_{app}) can be expressed as [24],

$$K_{\mathrm{app}} = K_{\mathrm{pw}} / \left(1 + C_{\mathrm{POM}} K_{\mathrm{POM/water}} + C_{\mathrm{DOM}} K_{\mathrm{DOM/water}}\right) \qquad (4)$$

where C_{POM} and C_{DOM} are the concentrations of POM and DOM, respectively, in water [$\mathrm{kg_{OM}/L_{water}}$], and $K_{\mathrm{POM/water}}$ and $K_{\mathrm{DOM/water}}$ are the respective sorption coefficients of the chemical [$\mathrm{L_{water}/kg_{OM}}$]. For highly hydrophobic chemicals, $K_{\mathrm{POM/water}}$ and $K_{\mathrm{DOM/water}}$ are large, and thus the denominator of Eq. (4) can be significantly >1, causing K_{app} to be smaller than K_{pw}.

Inorganic salts in water can cause a difference in sorption coefficients from pure water. Salts in water can induce a salting-out effect, which shifts the sorption equilibrium toward organic phases. The salting-out effect on the sorption coefficient can be described by using the Setschenow relationship [34],

$$\log\left(K_{\mathrm{plastic/salt\ water}} / K_{\mathrm{pw}}\right) = K^{\mathrm{s}} C_{\mathrm{salt}} \qquad (5)$$

where $K_{\text{plastic/salt water}}$ is the sorption coefficient from salt-containing water to plastic, K^{s} [M^{-1}] is the Setschenow coefficient, and C_{salt} is the concentration of the salt in M (e.g., ~0.5 M NaCl for seawater). K^{s} depends on the type of salt and the organic chemical of concern. Thus, the extent of salting-out effect (i.e., $K_{\text{plastic/salt water}}/K_{\text{pw}}$) depends on the type and the concentration of salt and the type of chemicals. In seawater, NaCl is largely responsible for the salting-out effect [35], and in NaCl solution, the salting-out effect increases with the molecular size and decreases with the polarity of the chemical [34]. The available data and models indicate that the sorption coefficients for HOCs in seawater can be higher by up to a factor of 2 in comparison to their K_{pw} in pure water [34, 36]. Thus, the effect of salt in seawater is rather minor.

2.5 Quantitative Models for Estimation of Sorption Coefficients

Experimental data for K_{pw} are available for only limited combinations of polymer and compound (see Sect. 3.5 below for some examples). Therefore, K_{pw} values often have to be estimated using a model. It must be noted that these models have been developed for unweathered, pure polymers and that their applicability to plastics that are weathered under marine conditions has to be explored.

The most common approach to estimate K_{pw} is a simple log–log correlation with K_{ow}, the octanol–water partition coefficient,

$$\log K_{\text{pw}} = \alpha \log K_{\text{ow}} + \beta \qquad (6)$$

Coefficients α and β are empirically calibrated using experimental data for K_{pw} and K_{ow}. Coefficients have been reported for several (pure) polymer types typical for marine litter [37, 38]. Such simple regression models are useful to estimate K_{pw} of chemicals that are structurally similar to the chemicals used to derive the regression coefficients. For example, a regression equation calibrated with data for PCBs is expected to provide sufficiently accurate predictions for other PCB congeners. However, predictions can be substantially less accurate for other chemicals because log K_{pw}–log K_{ow} correlations are not general for all chemicals.

A more general approach is to use a multiparameter model that explicitly considers the contributions of various intermolecular interactions to log K_{pw}. Such models are referred to as polyparameter linear free energy relationships (PP-LFERs). Among others, Abraham's linear solvation energy relationships (LSERs) are used most frequently [39]. LSERs for plastic–water sorption coefficients appear

$$\text{Log} K_{\text{pw}} = c + e\,E + s\,S + a\,A + b\,B + v\,V \qquad (7)$$

E, *S*, *A*, *B*, and *V* are the solute descriptors, describing the chemical ability to undergo molecular interactions. *E* is the excess molar refraction, *S* is the solute dipolarity/polarizability, *A* is the solute H-bond donor property, *B* is the solute H-bond acceptor property, and *V* is the molar volume. The lowercase letters in Eq. (7) are regression coefficients, indicating the differences in the complementary interaction properties between plastic and water. In comparison to single parameter models, PP-LFERs are more general in that they can be applied to practically any neutral chemical irrespective of its chemical class. Prediction errors are typically <0.3 log units [40, 41]. The descriptors are available for several thousands of compounds [42]. The current limitation of PP-LFERs to be used for plastic sorption is that the regression coefficients are unavailable for plastic types occurring frequently in the environment, which signifies an important future research topic.

While the models shown above always require empirical descriptors and fitting coefficients, there are also estimation models that only require the molecular structures of polymer and chemical as input. The COSMO*therm* program, based on the COSMO-RS theory, uses a quantum-mechanically calculated surface electron density of the molecule to describe the intermolecular interaction forces and derives partition coefficients via thermodynamic calculations [43]. The application of COSMO*therm* for polymer sorption has been reported before [44]. Another predictive approach is SPARC, which calculates partition coefficients using molecular descriptors that are derived solely from the molecular structure [45]. SPARC's calculations of molecular descriptors are based on group contribution methods with a diverse calibration data set. Both COSMO*therm* and SPARC are commercial software. The strong advantage of COSMO*therm* and SPARC is that predictions are possible for virtually any neutral chemical and any phase, provided that the chemical and the phases have defined molecular structure. The prediction accuracy is within 1 log unit on average [46] and often poorer than empirical fit models if the empirical models are used within their domain of applicability.

3 Sorption to Marine Plastics

3.1 Marine Plastics

The partitioning of hydrophobic chemicals to pristine, unaltered plastics has been studied extensively in the framework of developing passive samplers (e.g., [37]). However, in the marine environment, sorption could become dependent on the state of the plastic, which changes over time and place. For example, the role of polymer degradation (weathering) [5, 47], fouling, i.e., biofilm formation or organic matter fouling [11, 48] and competition [13] in the plastic sorption have been discussed in the literature. This implies that "marine plastic" constitutes a mixture of polymer types, with a range of sizes and ages, causing a distribution of sorption affinities even at small spatial scales. This also implies that making inferences on equilibrium sorption from field observations is challenging, due to long equilibration times [4, 5, 9] and a high variability in age and characteristics of microplastics found on the same location (e.g., [4, 9, 49]). Furthermore, this may limit the applicability of the model approaches mentioned in the previous section, which is limited to well-defined pure polymers with properties staying constant over space and time. In the following sections, effects of degradation and fouling will be discussed, and a comparison of in situ sorption coefficients with those for passive samplers will be provided.

3.2 Effects of Biotic and Abiotic Degradation on Equilibrium Sorption to Marine Plastics

In the marine environment, fragmentation of microplastic leads to smaller sized particles that eventually may reach the nano-scale [50, 51]. Polymers consist of a mixture of polymer chains with varying length. The chains are linked by weak secondary bonds like H-bond or vdW interactions or by physical interactions through entanglement of chains, leaving void space in between the chains. Polymer breakdown is mainly initiated by chemical reactions (oxidation) that makes the plastic brittle and the weak interactions are susceptible to breakage at a low energy level. In combination with other forces like friction, this causes formation of smaller polymer particles at the millimeter, micrometer, and nanometer size range [51]. Especially at beaches, the combination of photo-oxidation by UV exposure, a high temperature and high humidity probably enhances fragmentation rates and reduces the size of the plastic particles [47]. The changes occurring in the particles may lead to changing equilibrium partition coefficients through different mechanisms. Mato et al. [3] and Endo et al. [4] discussed three mechanisms for changing sorption characteristics upon degradation of plastic pellets. Here, we extend their discussions on the three mechanisms with additional information from recent studies.

1. The aforementioned weathering of plastic leads to smaller particles, thus increasing the specific surface area of the particles. Moreover, small cracks developing on the surface will increase the microscopic surface area. Fotopoulou and Karapanagioti [47] observed slightly increased surface areas for beach eroded PP and PE. Increasing the surface area increases the adsorption capacity of the plastic, whereas it does not influence the bulk absorption. Velzeboer et al. [11] indeed observed higher sorption to nano-sized PS particles than to micrometer-sized PE, whereas this would be reversed if the particles had equal size.
2. UV-B photo-oxidation or microbial degradation increases the abundance of oxygen containing groups like carbonyl groups and therefore the polarity of the plastic, which will lead to a change of the sorption coefficients. The effect of overall polarity on partition coefficients has been well-established for natural

organic matter in the aquatic environment [52–54]. Fotopoulou and Karapanagioti [47] observed an increase in functional groups on the surface of beach eroded PE, leading to negative surface charge at seawater pH. Beached eroded PP, however, did not show an increase in functional groups on its surface, which illustrates the polymer specificity of the surface alterations.

3. Differences in crystallinity have been shown to explain the differences in partition coefficients among different types of polymers [27, 55], as well as differences in partition coefficients for the same polymer at different states of weathering. A rearrangement of the amorphous rubbery regions inside the polymer and an increase in crystallinity would cause a decrease in the equilibrium partition coefficient if sorption to the amorphous regions is stronger than to the crystalline regions. However, an increased crystallinity might also enhance overall sorption if the crystalline domain has a higher sorption coefficient. For instance, Karapanagioti and Klontza [5] observed higher distribution coefficients for eroded plastic pellets, which they attributed to increased crystallinity of the pellets due to weathering.

It follows from these mechanisms that they could have both positive and negative influences on K_{pw} and may partly compensate for each other. Endo et al. [4] assessed the relationship between the carbonyl index of beached PE pellets as a measure of weathering and PCB concentrations in the field-sampled plastic pellets, yet they did not find any relationship.

3.3 Effects of Biofouling on Equilibrium Sorption to Marine Plastics

Like any surface in the marine environment, plastic will be colonized with micro- and macroorganisms, a process referred to as biofouling (e.g., [56, 57]). Lobelle and Cunliffe [57] describe how biofilm formation, leading to biofouling, develops in four phases: adsorption of DOC, attachment of bacteria, attachment of unicellular eukaryotes, and attachment of larvae and spores. For the formation of biofilms, rather elaborate quantitative models are available, often focusing on marine snow (e.g., [58]). Biofilms may subsequently cause the attachment of invertebrates and algae, which further increases the degree of biofouling.

We are not aware of literature specifically addressing the effect of biofouling on sorption. However, the main effects may be inferred from sorption phenomena known to occur for similar natural particles or particle assemblages. Biofouling turns the polymer particle into a dual domain sorbent, i.e., a microplastic core with an outer shell of organic material. This is similar to mineral particles with an organic matter coating or to mineral particle aggregates held by organic matter, like suspended solids, marine snow, or sediment. Because the organic matter shields the polymer surface from the direct ambient water layer, sorption to the microplastic implies that this organic matter layer has to be passed. The overall kinetics of the process then may become dependent on the resistances to transfer in the polymer, in the biofilm, and in the aqueous boundary layer surrounding the biofilm coated microplastic particle, where the slowest transfer process will determine the overall sorption rate [48].

These sorption kinetics can be modeled using the concepts of intra-organic matter diffusion (see [24]), which however is beyond the scope of the present chapter.

Sorption equilibrium also can be expected to exhibit dual domain behavior, with total sorption being the sum of the sorption to the microplastic (i.e., Eq. 1) and the sorption to the organic matter. Note that the organic matter may be located on the outer surface of the polymer particle, as well as inside the macropores. The overall sorption coefficient for the fouled plastic particle, $K_{\text{fouled plastic/water}}$ [$\text{L}_{\text{water}}/\text{kg}_{\text{fouled plastic}}$], would be

$$K_{\text{fouled plastic/water}} = f_{\text{PL}} K_{\text{pw}} + f_{\text{OM}} K_{\text{OM}} \tag{8}$$

where f_{PL} and f_{OM} (−) are the mass fractions of plastic and organic matter (OM) in the fouled particle, respectively, and K_{OM} [$\text{L}_{\text{water}}/\text{kg}_{\text{OM}}$] are the sorption coefficient for the attached organic matter (including biofilm, attached algae, and invertebrates). As explained in Sect. 2.2, for glassy polymers or for polymers with a high crystallinity, sorption would not be linear and the first term in Eq. (8) may be replaced by a term accounting for Freundlich, Langmuir, or Polanyi–Manes sorption (e.g., [19]). Here, we provide the equation with nonlinear sorption to the plastic accounted for by a Freundlich isotherm:

$$K_{\text{fouled plastic/water}} = f_{\text{PL}} K_{\text{Fr}} C_{\text{w}}{}^{\text{n}-1} + f_{\text{OM}} K_{\text{OM}} \tag{9}$$

in which the notations are the same as for Eq. (3). K_{Fr} and n depend on the types and conditions of plastic as well as on the chemicals.

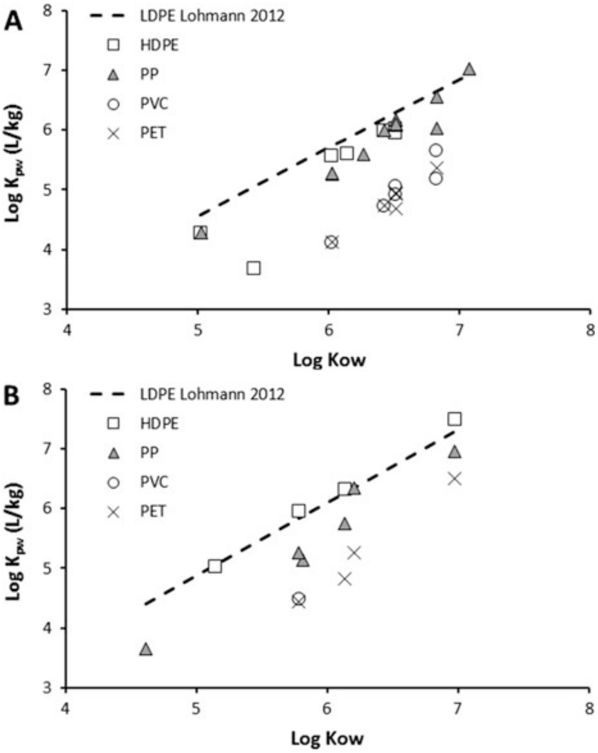
3.4 Sorption Competition

The sorption equilibrium to the plastic phase most probably is influenced by the presence of the organic matter, in case "adsorption" is the predominant mechanism of sorption. Attenuation of HOC sorption by organic matter fouling is well known for many geosorbents (e.g., black carbon, activated carbon) for which surface adsorption is the dominating mechanism (e.g., [59–61]). Velzeboer et al. [11] studied the effect of DOC on the simultaneous sorption of polychlorobiphenyls (PCBs) to microplastic and nano-sized plastic and observed no difference for micrometer-sized PE. This was explained from a partitioning (i.e., absorption) mechanism dominating sorption to the bulk of the plastic, which supports the additivity of sorption to plastic and OM as in Eq. (8). For 70 nm nano-PS, however, sorption generally was slightly lower in the presence of DOC, which suggests an adsorption mechanism and a sorption competition effect between DOC and PCBs. This also implies that the parameters in the first terms in Eqs. (8) and (9) depend on the concentrations of DOC and other competitors in the water. Apparent competition was also observed for sorption of phenanthrene and DDT to PVC and PE microplastic, i.e., phenanthrene sorption was lower at higher DDT concentrations in the study by Bakir et al. [13]. The studies are difficult to compare, however, because Velzeboer et al. [11] used 10–1,000 times lower aqueous phase concentrations and 6 weeks of equilibration instead of the 72 h used by Bakir et al. [13]. Several studies have shown long equilibration times for HOCs sorption to microplastics [3, 9, 62], suggesting that the data for 72 h may not fully relate to sorption equilibrium.

3.5 "In-Situ" Values of Sorption Coefficients

Data on sorption of HOCs to marine plastics under in situ conditions is important in order to assess the role of microplastics in transport and bioaccumulation of HOCs [17, 18]. As mentioned above, field-monitoring data of concentrations in marine plastics are not useful to obtain sorption coefficients, because of a tremendously large variability of plastic types, age, weathering state, fouling, and the extent of equilibration that occurs in the field. Field-exposure tests would provide insightful results, yet such data is very limited. In situ values for sorption coefficients can be calculated from chemical concentrations in plastic and ambient seawater, under equilibrium conditions (Eq. 1). Measurement of in situ sorption coefficients thus requires long exposure times [3, 9, 62]. Long exposure times also allow the weathering and fouling of the plastic, which further maximizes the relevance of the in situ values. To our knowledge, only one study measured chemical concentrations in plastic and ambient seawater after field tests [3]. They observed rapid uptake of various HOCs by plastic pellets in 6 days but concluded that this time was insufficient to reach equilibrium. Estimates of in situ PCB and PAH partition coefficients for LDPE, HDPE, PP, PET, and PVC can be inferred from long term sorption data provided by Rochman et al. [9], who measured the uptake of PCB and PAH by these polymers under controlled conditions in San Diego Bay. Uptake was measured up to 12 months and equilibrium concentrations were inferred from the uptake curves using a one-compartment two-parameter kinetic model. While Rochman et al. [9] did not directly measure HOC concentrations in seawater, we argue that the LDPE microplastic deployed for 1 year by Rochman et al. [9] can be considered as a regular passive sampler. The apparent aqueous phase concentrations in San Diego Bay can be calculated using previously published LDPE–water partition coefficients for passive samplers. Subsequently, the partition coefficients for HDPE, PP, PET, and PVC can be calculated using the calculated aqueous phase concentrations and the polymer phase concentrations reported by Rochman et al. [9] (Fig. 1). The validity of this approach is supported by the following. Previous studies using passive samplers used similarly long deployment times of, for instance, 60 days (LDPE [63]) up to 365 days (LDPE [64]). Furthermore,

Fig. 1 In situ log K_{pw} as a function of log K_{ow} for five polymers, for PCBs (panel **a**) and PAHs (panel **b**), based on data by Rochman et al. [9], observed uniformity of partitioning to LDPE among passive samplers [37] and between LDPE passive samplers and PE microplastics in the laboratory [11, 62]



sorption kinetic behavior could be described with the same parameters for up to 128 days (environmental PE pellets [62]), which would not be the case if discernable weathering would occur within these time frames. Lohmann [37] reviewed the literature on HOC partitioning to LDPE and concluded that values for the various LDPE materials were very close, and that the thickness of the LDPE had no influence on the equilibrium partition coefficients. This can be explained from the fact that LDPE has a relatively low crystallinity and therefore linear sorption to the amorphous, rubbery polymer fraction dominates. This also explains that Velzeboer et al. [11] measured Log K_{pw}–Log K_{ow} regression parameters for HDPE microplastic particles in seawater that agreed very well to the regression provided by Lohmann [37], an agreement also observed by Lee et al. [38]. The observed similarity among LDPE passive sampler materials and the similarity observed between LDPE microplastic and sampler materials mean that variation across PE materials apparently has a limited effect on K_{pw}, which also implies that the LDPE employed by Rochman et al. [9] can be assumed to have the same equilibrium sorption behavior.

It appears that the five polymers LDPE, HDPE, PP, PVC, and PET show different in situ partition coefficients (Fig. 1), and that the patterns are identical for PCBs (Fig. 1a) and PAHs (Fig. 1b). Taking LDPE as a reference with the highest values, it appears that HDPE has very similar K_{pw} values, whereas the other polymers have log K_{pw} values that are ~0.3–0.5 log units (PP) and ~1–1.5 log units (PVC and PET) lower than the values for LDPE. Regressions of log K_{pw} against log K_{ow} (not shown) were all linear and highly significant.

A couple of studies that measured relative differences in either HOC concentrations sampled from the same locations or K_{pw} between polymer types can be compared with the data from field-exposure tests in Fig. 1. Endo et al. [4] as well as Hirai et al. [8] measured PCB concentrations in marine plastic pellets and found concentrations that tended to be higher in PE pellets than in PP pellets sampled from the same location, which is consistent with the difference shown in Fig. 1. Karapanagioti and Klontza [5] performed laboratory phenanthrene sorption studies with equilibration up to 164 days and observed K_{pw} values for virgin PE being an order of magnitude higher than for PP. Two visually identically plastic eroded pellets however showed different K_{pw} values, illustrating the indeterminate nature of randomly sampled pellets. In short term (only 72 h) sorption experiments, Bakir et al. [13] found apparent phenanthrene sorption coefficients to virgin PVC being 1.5 orders of magnitude lower than those for PE, which also agrees to the difference between PE and PVC in Fig. 1. Lee et al. [38] measured K_{pw} values for PAHs, chlorobenzenes (CBs), and hexachlorocyclohexanes (HCHs) to "pure" HDPE, PP, and PS, in the laboratory. They found consistent correlations with log K_{ow} for PAHs and CBs, whereas for the HCHs relatively low K_{pw}'s were observed due to the polarity of the HCHs. LDPE again showed higher K_{pw} values than PP, whereas PS-K_{pw} values were even higher for low-molecular-weight PAHs and CBs and only for high-molecular-weight PAHs, PE showed the highest K_{pw} values.

In summary, our re-interpretation of the data from Rochman et al. [9] shows that the relative partition coefficients of various plastic types after 1-year in situ exposure experiments are consistent with the available literature data based on the laboratory experiments. Thus, LDPE and HDPE show the highest affinity for sorption of HOCs like PCBs and PAHs, followed by PP and then PET and PVC, a conclusion drawn earlier by Rochman et al. [9]. Therefore, we tentatively conclude that influences of weathering and fouling on sorption coefficients are insignificant within a 1-year exposure time. Further research is needed to address the effects of even longer time exposure on sorption properties and also in varying environmental conditions.

3.6 *Nanoplastic*

Nanoplastic is probably the least known area of marine litter but potentially also is the most hazardous [51]. For nano-sized plastics, some specific features may affect sorption, such as its extremely high specific surface area, and aggregation. We are aware of one study of HOC sorption to nanoplastics. Velzeboer et al. [11] investigated the simultaneous sorption of 17 PCBs to 70 nm polystyrene particles, which was compared with sorption to PE microplastic, sediment, fullerenes, and multiwalled carbon nanotubes. K_{pw} values for the nano-PS reached values up to 10^9 L/kg, which was much higher than values observed for micrometer-sized PE or bulk PS. PS is an aromatic polymer made from the monomer styrene. The strong sorption therefore was explained by hydrophobic interactions and π−π-interactions between PCBs and the aromatic PS, as well as by the very high surface area of the nano-PS, compared to micrometer-sized plastic. Isotherms were concave or S-shaped, which might have been caused by changes in aggregation state with increasing aqueous PCB concentration.

4 Conclusions and Outlook

Experimental K_{pw} data are rarely available for marine-plastic relevant polymers other than PE. Accordingly, well-calibrated empirical models to predict K_{pw} are available for PE only. Further sorption studies for other types of polymers are warranted. Particularly, glassy polymers such as PS and PVC need more attention because of their more complicated sorption behavior than rubbery polymers. The first results for nano-PS demonstrated strong sorption for PCBs and may have implications for its hazard. Uptake of micro- or nano-sized particles across cell membranes may cause particle toxicity as well as chemical toxicity (e.g., [65]). Thorough studies on the relationship between the size and the sorption properties should shed more light on possible mechanisms of enhanced sorption. While most studies have used PCBs or PAHs as test chemicals, other HOCs such as polybrominated diphenyl ethers, phosphate esters, and phthalate esters are also relevant because of their use for plastic additives. Extending the diversity of test chemicals will enlarge the applicability domain of K_{pw}-prediction models toward more chemical types and will also contribute to improved understanding of chemical–plastic molecular interactions. Influences of plastic degradation and fouling on K_{pw} have been conceptualized, although they still remain to be validated and quantified by experiments.

References

1. Carpenter EJ, Anderson SJ, Harvey GR, Miklas HP, Peck BB (1972) Polystyrene spherules in coastal waters. Science 178(4062):749–750
2. Gregory MR (1978) Accumulation and distribution of virgin plastic granules on New Zealand beaches. N Z J Mar Freshw Res 12(4):399–414
3. Mato Y, Isobe T, Takada H, Kanehiro H, Ohtake C, Kaminuma T (2001) Plastic resin pellets as a transport medium for toxic chemicals in the marine environment. Environ Sci Technol 35 (2):318–324
4. Endo S, Takizawa R, Okuda K, Takada H, Chiba K, Kanehiro H, Ogi H, Yamashita R, Date T (2005) Concentration of polychlorinated biphenyls (PCBs) in beached resin pellets: variability among individual particles and regional differences. Mar Pollut Bull 50(10):1103–1114
5. Karapanagioti HK, Klontza I (2008) Testing phenanthrene distribution properties of virgin plastic pellets and plastic eroded pellets found on Lesvos island beaches (Greece). Mar Environ Res 65(4):283–290

6. Ogata Y, Takada H, Mizukawa K, Hirai H, Iwasa S, Endo S, Mato Y, Saha M, Okuda K, Nakashima A, Murakami M, Zurcher N, Booyatumanondo R, Zakaria MP, Dung LQ, Gordon M, Miguez C, Suzuki S, Moore C, Karapanagioti HK, Weerts S, McClurg T, Burres E, Smith W, Van Velkenburg M, Lang JS, Lang RC, Laursen D, Danner B, Stewardson N, Thompson RC (2009) International pellet watch: global monitoring of persistent organic pollutants (POPs) in coastal waters. 1. Initial phase data on PCBs, DDTs, and HCHs. Mar Pollut Bull 58(10):1437–1446
7. Teuten EL, Saquing JM, Knappe DRU, Barlaz MA, Jonsson S, Björn A, Rowland SJ, Thompson RC, Galloway TS, Yamashita R, Ochi D, Watanuki Y, Moore C, Viet PH, Tana TS, Prudente M, Boonyatumanond R, Zakaria MP, Akkhavong K, Ogata Y, Hirai H, Iwasa S, Mizukawa K, Hagino Y, Imamura A, Saha M, Takada H (2009) Transport and release of chemicals from plastics to the environment and to wildlife. Philos Trans R Soc B Biol Sci 364 (1526):2027–2045
8. Hirai H, Takada H, Ogata Y, Yamashita R, Mizukawa K, Saha M, Kwan C, Moore C, Gray H, Laursen D, Zettler ER, Farrington JW, Reddy CM, Peacock EE, Ward MW (2011) Organic micropollutants in marine plastics debris from the open ocean and remote and urban beaches. Mar Pollut Bull 62(8):1683–1692
9. Rochman CM, Hoh E, Hentschel BT, Kaye S (2013) Long-term field measurement of sorption of organic contaminants to five types of plastic pellets: implications for plastic marine debris. Environ Sci Technol 47(3):1646–1654
10. Rochman CM, Hoh E, Kurobe T, Teh SJ (2013) Ingested plastic transfers hazardous chemicals to fish and induces hepatic stress. Sci Rep 3:3263
11. Velzeboer I, Kwadijk CJ, Koelmans AA (2014) Strong sorption of PCBs to nanoplastics, microplastics, carbon nanotubes, and fullerenes. Environ Sci Technol 48(9):4869–4876
12. Fries E, Zarfl C (2012) Sorption of polycyclic aromatic hydrocarbons (PAHs) to low and high density polyethylene (PE). Environ Sci Pollut Res Int 19(4):1296–1304
13. Bakir A, Rowland SJ, Thompson RC (2012) Competitive sorption of persistent organic pollutants onto microplastics in the marine environment. Mar Pollut Bull 64(12):2782–2789
14. Zarfl C, Matthies M (2010) Are marine plastic particles transport vectors for organic pollutants to the Arctic? Mar Pollut Bull 60(10):1810–1814
15. Gouin T, Roche N, Lohmann R, Hodges G (2011) A thermodynamic approach for assessing the environmental exposure of chemicals absorbed to microplastic. Environ Sci Technol 45 (4):1466–1472
16. Besseling E, Wegner A, Foekema EM, van den Heuvel-Greve MJ, Koelmans AA (2013) Effects of microplastic on fitness and PCB bioaccumulation by the lugworm Arenicola marina (L.). Environ Sci Technol 47(1):593–600
17. Koelmans AA, Besseling E, Wegner A, Foekema EM (2013) Plastic as a carrier of POPs to aquatic organisms: a model analysis. Environ Sci Technol 47(14):7812–7820
18. Koelmans AA, Bakir A, Burton GA, Janssen CR (2016) Microplastic as a vector for chemicals in the aquatic environment: critical review and model-supported reinterpretation of empirical studies. Environ Sci Technol 50(7):3315–3326. doi:10.1021/acs.est.5b06069
19. Allen-King RM, Grathwohl P, Ball WP (2002) New modeling paradigms for the sorption of hydrophobic organic chemicals to heterogeneous carbonaceous matter in soils, sediments, and rocks. Adv Water Resour 25(8-12):985–1016
20. Chiou CT (2002) Partitioning and adsorption of organic contaminants in environmental systems. Wiley, Hoboken
21. Adams RG, Lohmann R, Fernandez LA, MacFarlane JK, Gschwend PM (2007) Polyethylene devices: passive samplers for measuring dissolved hydrophobic organic compounds in aquatic environments. Environ Sci Technol 41(4):1317–1323
22. Hale SE, Martin TJ, Goss K-U, Arp HPH, Werner D (2010) Partitioning of organochlorine pesticides from water to polyethylene passive samplers. Environ Pollut 158(7):2511–2517
23. Xia G, Ball WP (1999) Adsorption-partitioning uptake of nine low-polarity organic chemicals on a natural sorbent. Environ Sci Technol 33(2):262–269

24. Schwarzenbach RP, Gschwend PM, Imboden DM (2003) Environmental organic chemistry, 2nd edn. Wiley, New York
25. Goss K-U, Schwarzenbach RP (2003) Rules of thumb for assessing equilibrium partitioning of organic compounds: successes and pitfalls. J Chem Educ 80(4):450–455
26. Carraher CE (2011) Carraher's polymer chemistry, 8th edn. CRC Press/Taylor & Francis Group, Boca Raton
27. Guo X, Wang X, Zhou X, Kong X, Tao S, Xing B (2012) Sorption of four hydrophobic organic compounds by three chemically distinct polymers: role of chemical and physical composition. Environ Sci Technol 46(13):7252–7259
28. Suzuki H, Grebowicz J, Wunderlich B (1985) Glass transition of poly(oxymethylene). Br Polym J 17(1):1–3
29. Berens AR (1978) Analysis of transport behavior in polymer powders. J Membr Sci 3(2):247–264
30. Xing B, Pignatello JJ (1997) Dual-mode sorption of low-polarity compounds in glassy poly (vinyl chloride) and soil organic matter. Environ Sci Technol 31(3):792–799
31. Xia G, Pignatello JJ (2001) Detailed sorption isotherms of polar and apolar compounds in a high-organic soil. Environ Sci Technol 35(1):84–94
32. Sander M, Lu Y, Pignatello JJ (2006) Conditioning-annealing studies of natural organic matter solids linking irreversible sorption to irreversible structural expansion. Environ Sci Technol 40 (1):170–178
33. Booij K, Hofmans HE, Fischer CV, Van Weerlee EM (2003) Temperature-dependent uptake rates of nonpolar organic compounds by semipermeable membrane devices and low-density polyethylene membranes. Environ Sci Technol 37(2):361–366
34. Endo S, Pfennigsdorff A, Goss K-U (2012) Salting-out effect in aqueous NaCl solutions: trends with size and polarity of solute molecules. Environ Sci Technol 46(3):1496–1503
35. Xie W-H, Shiu W-Y, Mackay D (1997) A review of the effect of salts on the solubility of organic compounds in seawater. Mar Environ Res 44(4):429–444
36. Jonker MTO, Muijs B (2010) Using solid phase micro extraction to determine salting-out (Setschenow) constants for hydrophobic organic chemicals. Chemosphere 80(3):223–227
37. Lohmann R (2012) Critical review of low-density polyethylene's partitioning and diffusion coefficients for trace organic contaminants and implications for its use as a passive sampler. Environ Sci Technol 46(2):606–618
38. Lee H, Shim WJ, Kwon JH (2014) Sorption capacity of plastic debris for hydrophobic organic chemicals. Sci Total Environ 470–471:1545–1552
39. Abraham MH, Ibrahim A, Zissimos AM (2004) Determination of sets of solute descriptors from chromatographic measurements. J Chromatogr A 1037(1–2):29–47
40. Endo S, Droge STJ, Goss K-U (2011) Polyparameter linear free energy models for polyacrylate fiber-water partition coefficients to evaluate the efficiency of solid-phase microextraction. Anal Chem 83(4):1394–1400
41. Endo S, Hale SE, Goss K-U, Arp HPH (2011) Equilibrium partition coefficients of diverse polar and nonpolar organic compounds to polyoxymethylene (POM) passive sampling devices. Environ Sci Technol 45(23):10124–10132
42. Endo S, Goss K-U (2014) Applications of polyparameter linear free energy relationships in environmental chemistry. Environ Sci Technol 48(21):12477–12491
43. Klamt A (1995) Conductor-like screening model for real solvents: a new approach to the quantitative calculation of solvation phenomena. J Phys Chem 99(7):2224–2235
44. Goss K-U (2011) Predicting equilibrium sorption of neutral organic chemicals into various polymeric sorbents with COSMO-RS. Anal Chem 83(13):5304–5308
45. Hilal SH, Karickhoff SW, Carreira LA (2004) Prediction of the solubility, activity coefficient and liquid/liquid partition coefficient of organic compounds. QSAR Comb Sci 23(9):709–720
46. Stenzel A, Goss K-U, Endo S (2014) Prediction of partition coefficients for complex environmental contaminants: validation of COSMOtherm, ABSOLV, and SPARC. Environ Toxicol Chem 33(7):1537–1543

47. Fotopoulou KN, Karapanagioti HK (2012) Surface properties of beached plastic pellets. Mar Environ Res 81:70–77
48. Fotopoulou KN, Vakros J, Karapanagioti HK (2014) Surface properties of marine microplastics that affect their interaction with pollutants and microbes. CIESM Workshop Monographs 46, Marine litter in the Mediterranean and Black Seas, Monaco
49. Turner A, Holmes L (2011) Occurrence, distribution and characteristics of beached plastic production pellets on the island of Malta (central Mediterranean). Mar Pollut Bull 62 (2):377–381
50. Andrady AL (2011) Microplastics in the marine environment. Mar Pollut Bull 62 (8):1596–1605
51. Koelmans AA, Besseling E, Shim WJ (2015) Nanoplastics in the aquatic environment. Critical review. In: Bergmann M, Gutow L, Klages M (eds) Marine anthropogenic litter. Springer, pp 325–340. doi:10.1007/978-3-319-16510-3_12
52. Xing B, McGill WB, Dudas MJ (1994) Sorption of α-naphthol onto organic sorbents varying in polarity and aromaticity. Chemosphere 28(1):145–153
53. Xing B, McGill WB, Dudas MJ (1994) Cross-correlation of polarity curves to predict partition coefficients of nonionic organic contaminants. Environ Sci Technol 28(11):1929–1933
54. Koelmans AA, Gillissen F, Makatita W, Van Den Berg M (1997) Organic carbon normalisation of PCB, PAH and pesticide concentrations in suspended solids. Water Res 31 (3):461–470
55. Young TM, Weber WJ (1995) A distributed reactivity model for sorption by soils and sediments. 3. Effects of diagenetic processes on sorption energetics. Environ Sci Technol 29 (1):92–97
56. Ye S, Andrady AL (1991) Fouling of floating plastic debris under Biscayne Bay exposure conditions. Mar Pollut Bull 22(12):608–613
57. Lobelle D, Cunliffe M (2011) Early microbial biofilm formation on marine plastic debris. Mar Pollut Bull 62(1):197–200
58. Kiørboe T, Tang K, Grossart HP, Ploug H (2003) Dynamics of microbial communities on marine snow aggregates: colonization, growth, detachment, and grazing mortality of attached bacteria. Appl Environ Microbiol 69(6):3036–3047
59. Wigton A, Kilduff JE (2004) Modeling trichloroethylene adsorption by activated carbon preloaded with natural dissolved organic matter using a modified IAST approach. Environ Sci Technol 38(22):5825–5833
60. Koelmans AA, Meulman B, Meijer T, Jonker MT (2009) Attenuation of polychlorinated biphenyl sorption to charcoal by humic acids. Environ Sci Technol 43(3):736–742
61. Rakowska MI, Kupryianchyk D, Grotenhuis T, Rijnaarts HH, Koelmans AA (2013) Extraction of sediment-associated polycyclic aromatic hydrocarbons with granular activated carbon. Environ Toxicol Chem 32(2):304–311
62. Endo S, Yuyama M, Takada H (2013) Desorption kinetics of hydrophobic organic contaminants from marine plastic pellets. Mar Pollut Bull 74(1):125–131
63. Khairy M, Muir D, Teixeira C, Lohmann R (2014) Spatial trends, sources, and air-water exchange of organochlorine pesticides in the Great Lakes basin using low density polyethylene passive samplers. Environ Sci Technol 48(16):9315–9324
64. Hale SE, Werner D (2010) Modeling the mass transfer of hydrophobic organic pollutants in briefly and continuously mixed sediment after amendment with activated carbon. Environ Sci Technol 44(9):3381–3387
65. Kettler K, Veltman K, van de Meent D, van Wezel A, Hendriks AJ (2014) Cellular uptake of nanoparticles as determined by particle properties, experimental conditions, and cell type. Environ Toxicol Chem 33(3):481–492