A Thermodynamic Approach for Assessing the Environmental Exposure of Chemicals Absorbed to Microplastic

Todd Gouin,*† Nicola Roche,‡ Rainer Lohmann,† and Geoff Hodges†

†Safety and Environmental Assurance Centre, Unilever, Colworth Science Park, Sharnbrook, Bedfordshire, U.K., MK44 1LQ
‡Graduate School of Oceanography, University of Rhode Island, South Ferry Road, Narragansett, Rhode Island, 02882 United States

ABSTRACT: The environmental distribution and fate of microplastic in the marine environment represents a potential cause of concern. One aspect is the influence that microplastic may have on enhancing the transport and bioavailability of persistent, bioaccumulative, and toxic substances (PBT). In this study we assess these potential risks using a thermodynamic approach, aiming to prioritize the physicochemical properties of chemicals that are most likely absorbed by microplastic and therefore ingested by biota. Using a multimedia modeling approach, we define a chemical space aimed at improving our understanding of how chemicals partition in the marine environment with varying volume ratios of air/water/organic carbon/polyethylene, where polyethylene represents a main group of microplastic. Results suggest that chemicals with log $K_{OW} > 5$ have the potential to partition $>1\%$ to polyethylene. Food-web model results suggest that reductions in body burden concentrations for nonpolar organic chemicals are likely to occur for chemicals with log $K_{OW}$ between 5.5 and 6.5. Thus the relative importance of microplastic as a vector of PBT substances to biological organisms is likely of limited importance, relative to other exposure pathways. Nevertheless, a number of data-gaps are identified, largely associated with improving our understanding of the physical fate of microplastic in the environment.

INTRODUCTION

Societal demand for plastic material continues to increase, with global plastic manufacture and consumption estimated to be 308 million tonnes annually. It is notable that approximately 50% of all plastic used is for single-use disposable applications. In Europe, a combination of plastic recovery programs, including mechanical recycling, feedstock recycling, and energy recovery (i.e., combustion of waste for energy generation) have resulted in a recovery rate of only 39% of plastic waste generated in 2003. Relatively poor plastic recovery rates, combined with inappropriate disposal of plastic products, is thus a significant factor influencing the potential for plastic debris to enter the environment. Unfortunately, there is a paucity of data quantitatively assessing the release rates of plastic to the terrestrial and aquatic environments. Nevertheless, based on a number of semi-quantitative and/or qualitative assessments, the observation of plastic debris and its temporal and spatial accumulation, particularly in the marine environment, imply cause for concern.

Whereas a number of studies report the effects of macroplastic (>5 mm) on the marine environment (see for instance refs 3 and 12), concerns regarding the potential effects of microplastic (<5 mm) have only recently emerged. Emissions of microplastic to the global marine environment include both primary sources (as derived from hand and facial cleansers, cosmetic preparations, airblast cleaning media, and production waste from plastic processing plants) and secondary sources (derived from fragmentation of macro-plastic as a result of photodegradation and abrasion due to wave action). Based on observations that the amount of macro-plastic accumulating in the marine environment is rapidly increasing, it is reasonable to expect that secondary sources of microplastic will dominate its environmental occurrence. Nevertheless, several studies note that while primary sources of microplastic represent a relatively insignificant contribution to the microplastic litter present in the marine environment, the lack of understanding regarding its environmental fate and behavior in the global oceans warrants caution with respect to its use, while a quantitative understanding regarding the potential risks is evaluated. For instance, a number of hazards have been identified relating to the potential impact that microplastic derived from primary sources may have on the oceanic environment. Foremost among these is the potential for microplastic to act as a vector for persistent, bioaccumulative, and toxic substances (PBT). Consequently, given the lack of understanding regarding the environmental fate and ecotoxicological effects of microplastic, either derived from...
primary or secondary sources, there is clearly a need to identify appropriate scientific methods that might help quantify the potential environmental risks associated with this material.

In this study we investigate the environmental risks associated with microplastic, with an emphasis on assessing the interaction of PBT substances with microplastic material in the environment and its subsequent fate within a food-web model. This is achieved by first utilizing a thermodynamic approach that aims at assessing the equilibrium distribution of chemicals with varying physical—chemical properties within an illustrative model environment. The model environment includes a sensitivity analysis that constraints the influence of varying volume ratios of air, water, sediment, and polyethylene microplastic on partitioning behavior. Second, the study aims at predicting how consumption of microplastic by aquatic organisms, using a steady-state food-web model, might influence body-burden concentrations, with an emphasis on exploring which model parameters influence an increase or a decrease in body-burden levels as compared to a diet that does not include microplastic. Results from the largely thermodynamic approaches used in this study are then used to recommend how research might be directed to better address priority data gaps.

**METHODS**

**Equilibrium Partitioning.** It is well understood that plastic polymers, such as polyethylene, have the capacity to absorb hydrophobic organic chemicals (HOCs), which has resulted in suggestions for their use as passive samplers. Additionally, the mechanisms that influence sorption and desorption will depend on both the sorbent and sorbate properties. Consequently, developing methods to assess the kinetics of sorption/desorption and equilibrium partitioning to plastic polymeric material that may be emitted to the environment is essential for improving our understanding of how HOCs of concern may interact with marine microplastic litter. It is suggested that significant insight regarding these processes can be obtained from observations related to the calibration of plastic polymeric material used for passive samplers, such as the use of performance reference compounds (PRC) to assist in understanding the kinetics of sorption/desorption and the time required for the passive sampler to reach equilibrium. As a first screen for identifying the relative importance of how organic contaminants may interact with primary sources of microplastic, we have utilized a multimedia modeling approach, based on fugacity.

The multimedia unit world environment has been selected to represent a coastal marine system with dimensions consistent with the marine environment of the Northwestern Hawaiian Islands (360,000 km²), where it has been estimated that 50 tonnes of plastic debris are accumulating annually. In this model system the water column depth is 10 m, the sediment depth is 10 cm, and the height of the atmosphere is 1 km. Additionally, an open ocean environment is also modeled, using a similar area but assuming a water depth of 20 m and no sediment compartment. As an illustrative example, we have assumed a minimum volume of plastic of 55 m³, based on the observations of Dameron et al. This volume assumes that the density of plastic is approximately 0.9 g·cm⁻³, consistent with the density of low density polyethylene. If we further assume that this plastic material has the potential to accumulate, consistent with observations of the accumulation of microplastic in the waters between Iceland and the British Isles prior to the 1990s, we can investigate how changes in volume ratios between water and plastic influence the partitioning of HOCs. For instance, a recent study reports that the maximum mass of plastic debris in the North Atlantic Subtropical Gyre is approximately 1100 tonnes, or about 1200 m³.

To give context with respect to the amount of primary microplastic emitted to the aquatic environment, based on the usage of polyethylene microplastic beads used in personal care products, we estimate that the per capita consumption of microplastic used in personal care products for the U.S. population is approximately 2.4 mg·person⁻¹·d⁻¹ (Supporting Information). The U.S. population is thus emitting 263 tonnes·yr⁻¹ polyethylene microplastic. This amount represents approximately 25% of the mass of plastic estimated to be present in the North Atlantic Subtropical Gyre. Given the wide dispersive use of microplastic used in personal care products across the U.S., it is thus believed that the volumes of plastic used in the illustrative multimedia model of 55 and 1200 m³ are representative of both ambient and worst-case scenarios, respectively.

**Chemical Space Diagrams.** We propose that a key component of understanding how chemicals might interact in the model environment described above is to discharge a suite of hypothetical HOCs with varying partitioning properties to an environment in which thermodynamic equilibrium between media is assumed, and there are no advective losses. This is essentially a Level 1 model, as described by Mackay. Using a graphical approach, analogous to Gouin et al., we can estimate the mass of organic carbon (M_OC) to which HOCs will absorb based on their relationship with the organic carbon to water partition coefficient (K_OC), which has units of L·kg⁻¹, as

\[ M_{OC} = \rho V_{sed} \varphi \]  

where \( \varphi \) is the fraction of organic carbon in the sediment (0.04), and \( \rho \) is the sediment density (2400 kg·m⁻³).

At equilibrium the total mass of chemical (M) will be distributed as

\[ M = V_W C_W + V_A C_A + V_{PE} C_{PE} + M_{OC} C_{OC} = C_W (V_W + K_{AW} V_A + K_{PE·W} V_{PE} + M_{OC} K_{OC}) \]  

where \( V \) is volume (m³), \( C \) is concentration (g·m⁻³), \( K_{AW} \) is the air-water partition coefficient, \( K_{PE·W} \) is the polyethylene-water partition coefficient, and the subscripts A, W, PE, and OC refer to air, water, polyethylene, and organic carbon, respectively. The mass fractions of the chemical in a particular medium (\( F_i \)) can thus be described as

\[ F_i = V_i K_{AW} / (K_{WW} V_W + K_{AW} V_A + K_{PE·W} V_{PE} + M_{OC} K_{OC}) \]  

where \( i \) represents A, W, or PE, and \( K_{WW} = 1.0 \). The fraction in organic carbon is described as

\[ F_{OC} = M_{OC} K_{OC} / (K_{WW} V_W + K_{AW} V_A + K_{PE·W} V_{PE} + M_{OC} K_{OC}) \]  

Consequently a plot of the mass fraction versus \( K_{OC} \) or \( K_{PE·W} \) and \( K_{AW} \) that considers the volume ratios of air, water, and organic carbon or polyethylene can be created to illustrate how chemicals might partition in the hypothetical marine environments described.

**Food Web Model.** Visualization of the interactions between PBT substances and various types of environmental media using the graphical approach described above is helpful as a screening tool.
tool to prioritize the properties of substances that have the greatest potential for sorption to microplastic. Prioritizing the properties of chemicals thus allows us to assess the fate and behavior of chemicals absorbed to microplastic within an organism and associated food-chain, with an emphasis on assessing the movement of chemicals from the plastic and across the walls of the gastrointestinal (GI) tract of an organism. To mimic how chemical substances that absorb to microplastic behave in a food-web, we have utilized the bioaccumulation food-web model described by Arnot and Gobas,32 which is freely available from the Trent University Centre for Environmental Modeling and Chemistry (CEMC) (http://www.trentu.ca/academic/aminas/enmodel) as the CEMC SFU AGRO model. It is notable that only the steady-state food-web component of the model has been utilized, i.e., the water quality model component has not been used, except to define a steady-state water concentration. The food-web includes several trophic levels, ranging from phytoplankton, zooplankton, benthos, forage fish, and a piscivorous fish. In the interest of brevity, discussion of model results will focus on the top predator organism (i.e., the piscivorous fish). The feeding matrix and input parameters for each of the organisms are given in the Supporting Information.

The food web model has been modified to include a polyethylene microplastic component of an organisms’ diet. The microplastic is modeled as an additional organism, which is a sphere with a diameter of 250 μm (8.2 × 10⁻⁶ cm³) and assumes that the polyethylene is equivalent to a 100% nonlipid organic matter (NLOM) fraction.

The uptake of chemicals in the model is based on a partitioning process between biota and water (\(K_{BW}\)):

\[
K_{BW} = v_{LB}K_{OW} + K_{OW}v_{NB}β + v_{WB}
\]

where \(v_{LB}\), \(v_{NB}\), and \(v_{WB}\) represent the lipid, NLOM, and water fractions of an organism, and \(β\) represents the sorption capacity of NLOM relative to octanol. Arnot and Gobas32 suggest a value for \(β\) of 0.035 for biological organisms, which implies that the sorption affinity of NLOM is 3.5% of octanol. In the case of plastics, we have assumed that the sorption capacity of the NLOM is 100% that of octanol. This is a conservative estimate based on results reported in a number of recent studies that demonstrate a linear relationship between \(K_{OW}\) and \(K_{PE,W}\) for HOCs.32,33 We note that for PBTs with polar functional groups, \(K_{PE,W}\) will be well below \(K_{OW}\),32 we thus overestimate the importance of microplastic as a vector for biological uptake for these substances.

Dietary assimilation efficiencies of lipid and NLOM are described in the model for zooplankton and aquatic invertebrates as being 72% and 75%, respectively.32 Whereas fish assimilations of lipid and NLOM are defined as 92% and 55%, respectively.32 It is notable that dietary assimilation efficiency describes the efficiency of the organism to digest lipid and NLOM. This parameter thus influences the uptake of chemical across the gastrointestinal tract by defining the fraction of chemical sorbed to lipid or NLOM that will be available for uptake. Uptake into the organism is described as a partitioning process, whereby a partition coefficient between the gastrointestinal tract and organism (\(K_{GW}\)) is defined as

\[
K_{GW} = (v_{LG}K_{OW} + K_{OW}v_{NG}β + v_{WG})/K_{BW}
\]

where \(v_{LB}\), \(v_{NB}\), and \(v_{WB}\) represent the lipid, NLOM, and water fractions of the gut contents of an organism, respectively.32 Thus, the results of the food-web model describe the uptake of chemical across the GI tract as a steady-state process, which therefore does not consider the kinetics of desorption of chemicals from the plastic. Kinetic factors that likely influence this process will be related to the gut retention time of the organism and the extraction efficiency of the gastrointestinal fluids for polyethylene plastic. A more sophisticated dynamic model would thus be required to directly assess desorption of chemicals from the plastic and uptake across the GI tract, with respect to time. Consequently, the model used in this study is limited to assessing the relative importance of exposure to chemicals from the natural diet versus digestion of plastic debris, and to identify potential data-gaps in our understanding using a steady-state food-web model.

To directly assess the influence of adding microplastic to the Arnot and Gobas32 bioaccumulation food-web model, we have modeled a suite of hypothetical organic chemicals with varying partition coefficients of one log unit of between 1 and 8 for \(K_{OW}\) and −4 and 2 for \(K_{AW}\). All chemicals are assumed to be perfectly persistent. The microplastic is assumed to be buoyant, and therefore resides in the water column, where it absorbs chemicals, based on their \(K_{OW}\) and is then consumed by organisms at a rate of 10% of an organisms’ diet. Differences in the chemical concentration for each of the organisms in the food-web with and without plastic are then derived as an estimate of the relative influence that inclusion of microplastic in an organisms’ diet may have on the bioaccumulation potential of an HOC.
RESULTS AND DISCUSSION

Equilibrium Partitioning and Chemical Space Diagrams. The volume ratio of air/water/organic carbon/polyethylene for the marine coastal environment is $6.6 \times 10^{12}:6.55 \times 10^{10}:1.26 \times 10^{7}:1$. Figure 1 is a plot of the mass fraction versus $\log K_{AW}$ and $\log K_{OC}$, which graphically illustrates the equilibrium partitioning space of a number of environmentally relevant chemicals for which measured $K_{OC}$ data are available, within the marine coastal environment defined in this study (Supporting Information). Only those substances with $\log K_{OC} > 5.5$ are likely to partition significantly (>99%) to organic carbon. Based on the volume ratios between organic carbon and polyethylene in this system, in which the organic carbon present in the system is $1.26 \times 10^7$ times greater than the polyethylene, it is reasonable to expect that the majority of partitioning in this system will be to the organic carbon fraction. Indeed, the results shown in Figure 1 do not include polyethylene because partitioning to polyethylene in this system is <0.1%, even for substances with $\log K_{PE-W} > 7$.

Figure 2a illustrates the equilibrium partitioning of 32 chemicals, for which measured $K_{PE-W}$ values are available, in an open-ocean environment with an air/water/polyethylene ratio of $3 \times 10^{11}:6.0 \times 10^{9}:1$ (i.e., volume of polyethylene = 1200 m$^3$). Results shown in Figure 2a suggest that, based on the relatively small volume of polyethylene in the environment, organic chemicals of environmental relevance partition between the air and water, with significant cycling between these two compartments. If we assume, however, that the amount of plastic in this system will continue to accumulate as a result of continuous discharge, then it is possible that the volume of plastic will increase to a level where a significant fraction of chemical may partition into it. Figure 2b illustrates the equilibrium partitioning in an open-ocean environment where the volume of plastic has increased by 3 orders of magnitude (i.e., $10^6$ m$^3$). In this system we begin to observe that substances with $\log K_{PE-W} > 5$ will now have the potential to partition >1% to polyethylene. Thus in a system where there are large quantities of plastic, and limited natural organic matter, significant partitioning of bioaccumulative HOCs into polyethylene plastic will occur. It is notable that this observation assumes that the presence of organic matter in the water, such as phytoplankton, is negligible. Where populations of phytoplankton are elevated, however, increased partitioning to the phytoplankton will likely occur, consistent with observations of Dachs et al., and thus the relative partitioning of HOCs to polyethylene will decrease accordingly.

The results in Figures 1 and 2 effectively illustrate the output of a sensitivity analysis, which highlights the relative importance of the volume ratios between air, water, naturally occurring organic carbon, and polyethylene plastic with respect to how the partitioning behavior of chemicals will change with varying volume ratios. The results clearly imply that increasing quantities of plastic will result in competition for the sorption of hydrophobic substances to...
naturally occurring organic carbon. Thus quantifying the amounts of plastic in the environment is needed to improve our understanding of the relative importance of this process. It is notable that since this is an equilibrium partitioning approach, the size of the plastic does not influence the results illustrated. Thus the results relate to both macro- and microplastic material. The time to equilibrium, however, will differ depending on the size of the material, with microplastic reaching equilibrium sooner than macroplastic.

It has been suggested that substances absorbed into plastic as a result of their partitioning behavior may be transported in the environment from source regions and may cause a negative impact on remote environments. Zarfl et al. have assessed the relative importance of this transport mechanism to the Arctic Ocean. Their results, however, suggest that this transport process, as compared with the transport of pollutants via atmospheric and oceanic currents, is orders of magnitude smaller.36 Thus, the movement of plastic is not likely to be a significant vector for transporting HOCs from source to remote regions.

Nevertheless, Zarfl et al. imply that it may be possible that highly hydrophobic organic chemicals (for instance log \(K_{ow}>6.5\)), which typically partition strongly to sediment, and therefore have limited transport potential, may have enhanced mobility if absorbed to buoyant microplastic material. Thus, concern regarding the relative importance of microplastic as a vector for PBT substances remains, particularly given the suggestion that an organism that consumes microplastic material, to which HOCs have absorbed, can result in enhanced uptake by the organism.16

Results illustrated in Figures 1 and 2 thus suggest that the potential for enhanced biological uptake, as a result of consuming microplastic, will likely be limited to chemicals with log \(K_{oc}/\log K_{ow}>6.5\), since these are the substances that have higher potential for partitioning to polyethylene plastic, and thus will have the greatest potential to cause a detrimental effect. It is notable, however, that gastrointestinal absorption efficiency of HOCs decreases beginning at about log \(K_{ow}>5.5\).16–37 Thus assessing an organism’s potential to extract highly HOCs of environmental concern, absorbed to microplastic, will be complicated by a number of competing processes, which are explored in greater detail below.

Simulating Biological Uptake and Bioaccumulation. Figure 3 illustrates the chemical space related to reductions in body burden concentrations associated with a piscivorous fish that includes a 10% microplastic component of its diet. The bioaccumulation of chemicals is shown to decline, with chemicals having log \(K_{ow}\) of between about 6.5 and 7.5 showing >20% reduction in body burden concentrations as a consequence of including 10% microplastic in the diet. Reductions in body burden concentrations are also observed to increase as the amount of microplastic in the diet increases.

The observation of reductions in body burden concentrations is due to the high sorption affinity assumed for polyethylene, which results in a fugacity gradient within the GI gut that does not favor transfer to the organism. For instance, organic matter that is degraded in the GI gut results in contaminant concentrations per mass of organic carbon, thus there is an increase in fugacity that favors transfer to the organism, if polyethylene is absent. If polyethylene is present in the GI gut, however, which is assumed to be nondegradable, then the fugacity increase will be less due to the sorption affinity of the plastic. Consequently, a reduced body burden concentration can be realized. This hypothesis is consistent with other studies that have demonstrated limited absorption efficiency related to the consumption of nondigestable material.38 Moser and McLachlan,38 for instance, observed that consumption of nondigestible fats, such as olestra, could be an efficient process for reducing chemical body burdens. Thus, the role of microplastic as a vector for enhanced biological exposure of PBT substances appears to be of limited importance.

Nevertheless, we further assess the potential for an increase in body burden concentrations by performing a sensitivity analysis on various input parameters defined in the food-web model. Figure 4 illustrates the results with respect to changing the dietary assimilation efficiency of NLOM and the percent lipid in prey fish consumed by the piscivorous fish.

Figure 4 illustrates that decreases in body burden mass are less pronounced in piscivorous fish that consumes microplastic along with prey with relatively low lipid content (1%) and which has an increasing potential to digest NLOM. This observation appears to be consistent with the hypothesis described earlier, in which the fugacity of a chemical within the GI gut of the organism can vary depending on the relative fractions of lipid and NLOM present in the system. Variability in the potential for the organism
to digest NLOM relative to lipid will thus further influence the fugacity of the chemical in the GI gut, and consequently the transfer of chemical to the organism. Consequently, the design of an experiment aimed at assessing the role of ingested microplastic as a vector for exposure to PBT substances needs to consider not only the kinetics related to the digestion efficiency of the plastic (such as gut residence time and gut extraction efficiency), but also the influence of the natural diet.

It is of interest to note that increasing the dietary assimilation efficiency to 95% results in negligible differences in body burden mass between an organism that consumes plastic and one that does not (Figure 4). This is due to the increased capacity of the organism to not only digest plastic polymeric material, but also the increased capacity to digest NLOM associated with its natural diet. Clearly, caution is warranted with respect to this discussion, since the environmental relevance of an organism that is highly efficient at digesting NLOM and which consumes a diet low in lipid content is likely limited.

**Addressing Limitations and Identifying Research Needs.**

The theoretical approaches used in this study largely assume thermodynamic equilibrium. Consequently, there is a need to better understand and assess the influence of kinetics with respect to sorption/desorption processes. For instance, what is the influence of rubbery to glass transition of the plastic on the Fickian diffusion of a chemical through the polymeric material? There are some studies that have demonstrated that chemical diffusion through polyethylene decreases with increased crystallinity, however, further research regarding the relevance of this process as it pertains to sorption/desorption of environmentally relevant chemicals of concern is needed. Additionally, there is a need for improving our understanding of how microbial biofouling influences sorption/desorption processes. From observations based on the use of PRC in passive samplers, for instance, it has been demonstrated that biofouling can significantly influence uptake rates, thus improving our understanding of how this process influences both the fate of the plastics and chemicals sorbed to the plastic and could enhance our ability to better assess the relative risk.

Apart from the capacity for plastic debris to sorb chemicals of concern, there is also a need to improve our understanding of the fate of the physical presence of the microplastic material in biological organisms. Specifically, what are the gut retention times and what fraction of microplastic consumed by an organism moves across the epithelial tissue into the organism? What influence does the size and shape of the microplastic have with respect to a toxicological response? Thus, while it appears that the role of microplastic as a vector for PBT substances may be relatively small when compared to other exposure pathways, it also the in...


