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Examining the Relevance of the Microplastic-Associated Additive Fraction in Environmental Compartments

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ABSTRACT: Plastic contamination is ubiquitous in the environment and has been related to increasing global plastic usage since the 1950s. Considering the omnipresence of additives in plastics, the risk posed by this contamination is related not only to the physical effects of plastic particles but also to their additive content. Until now, most routine environmental monitoring programs involving additives have not considered the presence of these additives still associated with the plastic they were added to during their production. Understanding environmental additive speciation is essential to address the risk they pose through their bioavailability and plastic-associated transport. Here, we present and apply a theoretical framework for sampling and analytical procedures to characterize the speciation of hydrophobic nonionized additives in environmental compartments. We show that this simple framework can help develop sampling and

sample treatment procedures to quantify plastic-associated additives and understand additive distribution between plastics and organic matter. When applied to concrete cases, internal consistency checks with the model allowed for identifying plastic-associated additives in a sample. In other cases, the plastic-organic carbon ratio and additive concentration in the matrix are key factors affecting the ability to identify plastic-associated additives. The effect of additive dissipation through diffusion out of plastic particles is also considered.

KEYWORDS: *microplastic, nanoplastic, plastic debris, contaminant, chemical additive, sorption, bioavailability, aquatic environment*
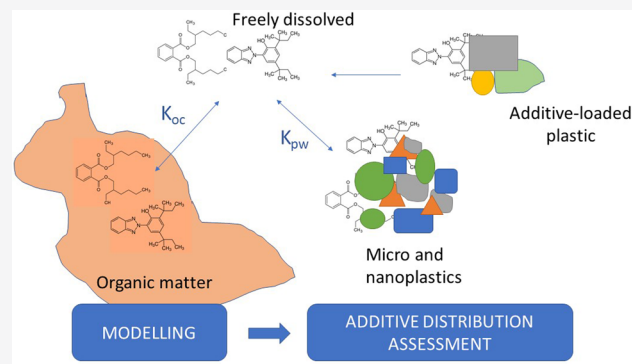
1. INTRODUCTION

Plastic debris carries a wide range of inorganic and organic chemicals in the environment.[1] While the direct toxic effect of plastic materials based on their polymeric nature is still debatable, a scientific consensus exists on their trojan horse effect. This effect is based on the plastic debris' impact related to the contaminants they may transport from the environment into organisms.[2] While microplastics can be relevant for some large living species, nanoplastics represent a class of plastic debris that is even more complex due to their high diffusion and ability to cross biological barriers. Some chemicals are sorbed to plastic debris during their life cycle in the environment in a way similar to other natural suspended materials. However, plastic materials are also known to contain a large range of organic and inorganic additives.

In some cases, the mass of additives can reach up to 35% of the plastic mass.[3] Additives may be released from the plastic through diffusion and partitioning processes governed by Fick's law.[4] Mechanical processes and photodegradation of the plastic debris can also be responsible for releasing additives.[5,6] It was demonstrated that physical processes form microplastics and nanoplastics (MNPs).[7] Many of these studies have focused so far on plastic debris that is relatively straightforward to

manipulate, separate, clean, and prepare for extraction. Yet, the contribution of additives present in microscale and nanoscale fractions of plastics debris has not been investigated. It is quite conceivable that the quantification of certain additives in abiotic matrices such as sediments in routine monitoring programs may have been due in part to the presence of additive-loaded plastics. In general, it is difficult to know whether an extraction procedure can access the entire pool of chemicals present in a sample. In the case of additives associated with plastic debris, ensuring an exhaustive extraction may even be more challenging.

This lack of data is clearly explained by the lack of understanding of the mechanisms of the plastic—additives interaction in natural media and the associated analytical methodologies. Such knowledge is mandatory to characterize the amounts of chemical additives associated with the MNPs

and released into the environment, such as from wastewater treatment plant effluents or run-off/stormwater. Besides the characterization of the presence of the additives related to MNPs, understanding the speciation of the chemical additives onto these new emerging carriers in the environment would help better predict the impact in both the short and long term. To tackle such challenges and before devoting intensive and costly analytical developments, theoretical and experimental approaches are needed to improve sampling and analysis and aid in interpreting the data. In the present study, we propose investigating the challenges mentioned above through a modeling exercise to assess the expected distribution of chemical additives in an environmental matrix or sample. This will directly contribute to the design of effective sampling and sample processing procedures for characterizing the presence of microplastic-associated chemical additives. Although plastic additives include diverse classes of chemicals such as metals, organometallic compounds, or ionizable substances, this study focuses exclusively on hydrophobic and nonionized substances, some of which are described in Table S1 in the Supporting Information.

2. METHODS

2.1. Model Development. In an abiotic sample related to the aquatic environment, the total sample mass (M_s) is distributed between the water (M_w), the particulate matter excluding plastics (M_{PM}), and the masses of the different plastics (M_P)

$$M_s = M_w + M_{PM} + M_{P1} + M_{P2} + ...M_{Px} \qquad (1)$$

where M_{P-T} is the total mass of all plastics in the sample. The total amount of chemical additive (N_{s-CAD}) is distributed between the water (N_{w-CAD}), the solid matter matrix (excluding plastics, N_{PM-CAD}), and the MNPs $(N_{Pn-CAD}$ with n from 1 to x number types of plastics)

$$N_{s-CAD} = N_{w-CAD} + N_{PM-CAD} + N_{P1-CAD} + N_{P2-CAD}$$
$$+ ...N_{Px-CAD} \qquad (2)$$

The fraction on a weight basis of plastic x in the total amount of plastic in the sample is f_{Px},

$$f_{Px} = \frac{M_{Px}}{M_{P-T}} \qquad (3)$$

and P the fraction of plastic in the sample (on a weight basis)

$$P = \frac{M_{P-T}}{M_s} \qquad (4)$$

Because for a specific polymer, not all microplastic particles will contain a particular chemical additive as an additive initially added during plastic production. P_{Px} can be expressed as the chemical additive-loaded mass of the plastic x in the total mass of the plastic p in the sample to relate the concentration of the chemical additive in the loaded-plastic (C_{CADx}) and the concentration of the chemical additive in the overall plastic P

$$C_{Px-CAD} = C_{CADx}P_p \qquad (5)$$

Equation 2 can then be rewritten

$$N_{s-CAD} = N_{w-CAD} + N_{PM-CAD} + C_{CAD1}f_{P1}P_{P1}Pf_{P1}$$
$$+ ...C_{CADx}f_{Px}P_{Px}Pf_{Px} \qquad (6)$$

The amount of a hydrophobic organic chemical additive sorbed to the particulate matter (C_{CAD-PM}) of a sample/matrix can be expressed as a function of the organic carbon (OC) content of the solid matrix f_{OC}, the freely dissolved concentration in water $(C_{CAD-free})$, and the organic carbon–water distribution coefficient (K_{OC}), so that N_{PM-CAD}

$$N_{PM-CAD} = M_{PM}f_{OC}K_{OC}C_{CAD-free} \qquad (7)$$

For simplicity, log K_{OC} can be set equal to log K_{ow}, which is a reasonable assumption considering the presence of amorphous OC.[8] For example, this first approximation seems appropriate for organophosphate flame retardants or phthalates.[9,10] In these studies, log K_{OC} was in good agreement with log K_{ow} values. This may not be valid for every situation encountered, and although log K_{OC} may correlate to log K_{ow}, they may not be equal. Much work has been conducted in the last two decades to improve organic-carbon water partition coefficients predictions for hydrophobic chemicals. Higher sorption can be expected in the presence of refractory OC, such as black carbon.

A final and possibly relevant additive fraction not accounted for in the mass balance above is the part that has sorbed from the environment to the (micro)plastic particles during the life/transport of the (micro)plastic. The sorption of nonionized and hydrophobic chemicals to plastic debris depends on the characteristics of the chemical itself and the properties of the plastic. In the case of glassy polymers, adsorption through surface processes governs the interaction, while for rubbery polymers, sorption takes place through partitioning. Adsorption may be characterized through linear or nonlinear isotherms with proportionally higher sorbed amounts at lower concentration levels in water.[11] The nature of the interaction also depends on the surface aging of the plastic. However, as a first approximation to predict sorbed amounts, equilibrium between the concentration of the chemical additive in the polymers/plastic and the freely dissolved concentration in water can be assumed. A polymer–water partition coefficient (K_{pw}) can be used to estimate the amount of a chemical sorbed to the plastic, which was not initially present in the plastic.[12−14] A specific K_{pw} could be used for each type of polymer for an additive. However, such data will not be available for many polymers and will be dependent on the properties of each polymer. We can express the mass of an additive sorbed to a plastic that was initially free of additive $(N_{sorb-CAD})$ using eq 8

$$N_{sorb-CAD} = M_{P-T}(1 - P_{P1}f_{P1}... - P_{Px}f_{Px})K_{pw}C_{CAD-free} \qquad (8)$$

In eq 8, we have simplified the sorption by considering a main polymer–water partition coefficient (K_{pw}) and not specific sorption to each type of plastic. Polymer–water adsorption or absorption coefficients are mostly available for the selected chemicals: polyethylene, polystyrene, and polypropylene.[15] Incorporating eqs 7 and 8 into eq 6 yields a model that describes the distribution of a chemical additive in an environmental sample containing microplastics. An excel spreadsheet was prepared according to the equations given above.

One other process that may need to be considered is the loss or release of additives from the plastic during its life and
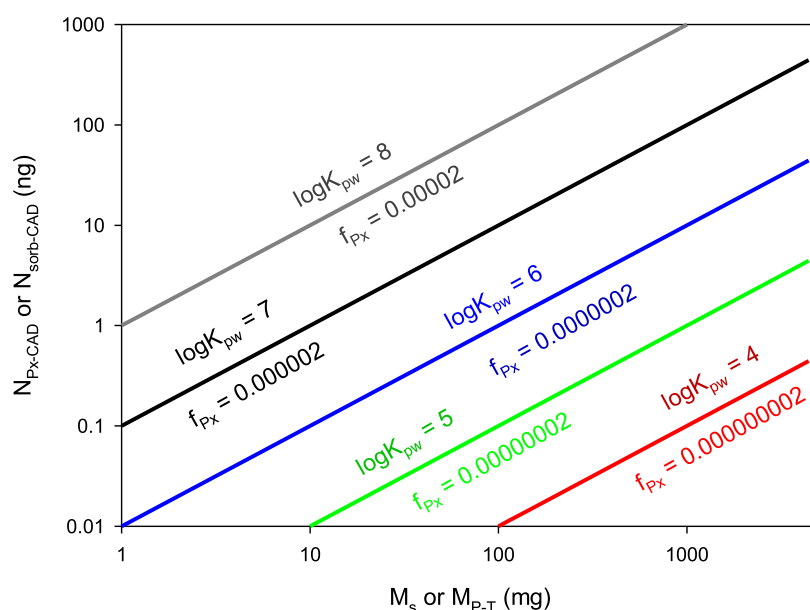
Figure 1. Simulated variation in the mass of the model plastic-incorporated or sorbed chemical additive (CAD) in a sample ($N_{Px\text{-}CAD}$ or $N_{sorb\text{-}CAD}$ in ng) as a function of the overall mass of plastic ($M_{P\text{-}T}$ in the range 1−5000 mg), of log K_{pw} of 4, 5, 6, 7, and 8 and of f_{Px} values of 0.00002, 0.000002, 0.0000002, 0.00000002, and 0.000000002. For this simulation, the $C_{CAD\text{-}free}$ was set to 0.01 ng L^{-1}, P_{Px} = 0.2, and the proportion of CAD in the plastic x = 5%.

degradation. Factors involved in this release of additives from microplastics include diffusion and polymer−water partition coefficients, MNPs particle shape and size, and/or the additive distribution within the plastic. The understanding and theoretical basis for the exchange of chemicals between polymers or MNPs and chemicals in water or other environmental matrices can be found elsewhere, such as in the passive sampling literature.[16−18] Additive dissipation processes will tend to lower concentrations in plastic debris until these reach equilibrium with $C_{CAD\text{-}free}$ in the environment they are present in. Limited data exist on the rates of losses of chemical additives during the lifetime of plastics. Over the last few years, experiments have been conducted to estimate the release rates of additives from microplastic particles.[19−21] In a previous study, we have used an analytical solution to the diffusion of a chemical in a sphere,[22] to predict the proportion of chemicals released from a microplastic particle in the gut of an organism in a worst-case scenario.[4] This model can also be used to predict whether a substantial loss of additives can be expected based on the residence time of additive-loaded microplastics in a specific matrix. While resistance to mass transfer external to the particle may be relevant to the loss/ release of additives, the main factors are internal, that is, the additive's diffusion coefficient in the polymer and the particle size or diameter. Other factors that may impact the release or loss of additives include microplastic particle erosion or ultraviolet (UV) light degradation.

3. RESULTS AND DISCUSSION

3.1. Simple Case of Mass of Plastic in the Sample Versus Mass of the Additive Present. The first simulations presented in Figure 1 show the amount of a model additive (N_{CAD} in ng) present as an additive or sorbed to the plastic from the environment the plastic was sampled from, as a function of the overall mass of plastic in the sample ($M_{P\text{-}T}$ in mg). Simulations were based on varying the proportion of additive-loaded plastic f_{Px} or the K_{pw} for a constant $C_{CAD\text{-}Free}$.

Interestingly, considering an analytical limit of detection (LOD)/limit of quantitation (LOQ) in the range of 0.1−1 ng per sample, a compound with log K_{pw} = 4 and a $C_{CAD\text{-}free}$ = 10 pg L^{-1} is unlikely to be detected if the mass of plastic sampled is below 1 g. The $C_{CAD\text{-}free}$ would have to be at the ng L^{-1} levels to be found in the plastic. Alternatively, this would mean that the chemical was present as an additive with an f_{Px} > 0.0000002. In the case of equilibrium, a very hydrophobic chemical, with log K_{pw} = 8, should be found above the LOD in as little as 1 to 10 mg of plastic, at $C_{CAD\text{-}Free}$ = 10 pg L^{-1}. Another way to read Figure 1 is to answer the question: what proportion of additive-loaded plastic must we have in our plastic sample to be able to measure it? If we have a sample with 10 mg of plastic, we are not likely to detect an additive loaded at 5% in the plastic with a proportion of f_{Px} < 0.000002. Despite the oversimplification (e.g., no additive release or dissipation) and assumptions (e.g., equilibrium conditions) made herein, these simulations must help distinguish whether additives measured above LOD may be present as additives or sorbed from the environment during the lifetime of the plastic.

For example, an analysis of single pieces of plastic pellets and fragments ingested by seabirds was undertaken by Tanaka et al.[23] They found a UV filter, UV-326, at the level of 180 μg g^{-1} of polyethylene in 2 fragments (1% of all fragments analyzed). Assuming a polyethylene−water partition coefficient in the range of log K_{ow} (i.e., 5.6), equilibration with a UV-326 concentration in water of 500 ng L^{-1} is needed to reach such a high concentration in the plastic fragment. This is not realistic for the North Atlantic or waters near Mukoji Island, where the freely dissolved concentration will be in the low pg L^{-1} range or below. The concentration reported in these polyethylene fragments is only a factor of 3−100 lower than the UV filter content used in PE or PP.[24] In this example, this compound was likely present in these fragments as an additive initially added to the plastic. The limits of detection for the additives investigated were close to the range of concentrations that
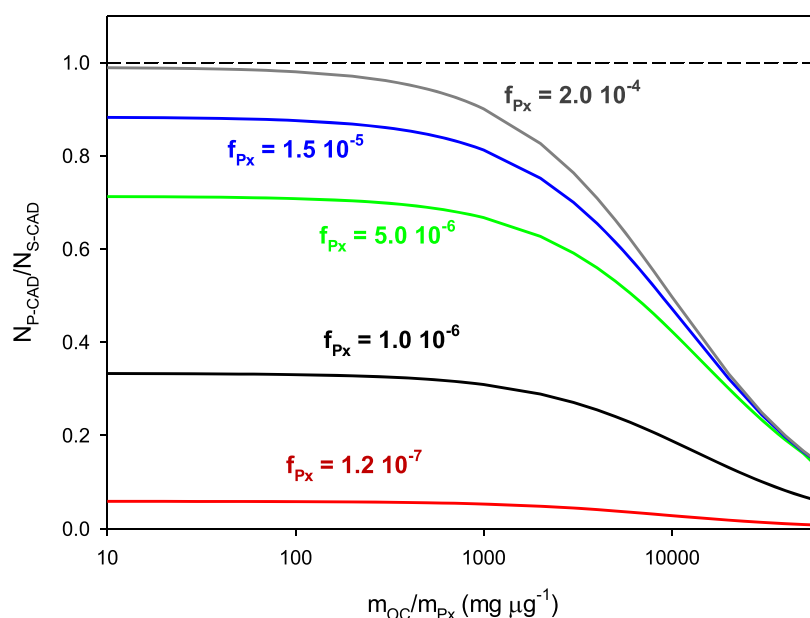
Figure 2. Simulated variation in the proportion of model plastic-incorporated chemical additive (CAD) in a sample ($N_{P\text{-}CAD}/N_{S\text{-}CAD}$) as a function of the organic carbon (OC) content to the plastic x ratio of the sample and the proportion of additive-loaded plastic f_{Px}. For this simulation, the $C_{CAD\text{-}free}$ was set to 1 ng L^{-1}, log K_{pw} K_{OC} = 5, P_{Px} = 0.001, P = 0.08, and the proportion of CAD in the plastic x = 5%.

would be expected in the case of additives sorbed to the plastic from water.

The extraction and analysis of additives in a single plastic fragment is possible when these fragments are sufficiently large. For other types of samples containing smaller plastic particles, the smaller the particles, the higher the number of particles that need to be extracted or preconcentrated during sample processing to obtain a sufficient mass of plastic for additive analysis. For example, considering reported concentrations of PE, PP, PVC, PS, or PMMA in the range of 0.5–2 mg g^{-1} dry weight in wastewater treatment plant biosolids,[25] the extraction of 1 g of biosolids would require an additive-loaded plastic content (5% additive or 50 ng μg^{-1} plastic) in the range of 0.01–0.1 μg to reach LOQ of conventional gas chromatography–mass spectrometric analysis for that additive. In other words, for this biosolid sample, an additive-loaded plastic content equivalent to under one-thousandth of the total amount of plastics in the sample is needed to detect the plastic-associated additive. In terms of particle size, that amount of plastic is equivalent to a single 60 μm additive-loaded particle or over 200 particles with a 10 μm-diameter.

The quantification of additives contained in plastics is increasingly being undertaken using the first thermal desorption step of a two-step pyrolysis-GC/MS analysis.[26] Because the sample mass that can be analyzed is at the mg or μg level, a substantially higher proportion of additive-loaded plastic needs to be present in the sample, indicating that a preconcentration step may be required before analysis.[27] In this case, low μg amounts of additive-loaded plastic need to be added to the pyrolysis-GC/MS sample cup to identify/quantify an additive. This is in the range of the LOD reported to analyze additives in plastic samples using pyrolysis-GC/MS.[28,29] For sorbed compounds, the challenge is even larger. For a compound such as the polycyclic aromatic hydrocarbon fluoranthene, generally found in European surface waters at concentrations around 1–10 ng L^{-1}, quantification above the LOD would require a generic plastic–water partition/

distribution coefficient log K_{pw} = 5 and the extraction and analysis of 1 mg of microplastic.

An interesting calculation estimates the number of additive-loaded microplastic particles of a specific size range that must be sampled to reach a LOQ of 1 ng g^{-1} of biosolids. Over 40 000 particles need to be sampled when working with 1 μm diameter. For larger particles with a diameter of 10 or 100 μm, either 40 or <1 additive-loaded particle would need to be sampled. Overall, these calculations demonstrate that the sampling step is important. A preconcentration step to concentrate plastic particles from the matrix may be required. For surface waters and wastewater treatment plant effluents, large volume (sequential) filtration or continuous-flow centrifugation can be put in place to extract a sufficient amount of suspended matter from water.[30] As discussed in one of the following sections, the next challenge is to consider the remaining matrix as a possible sorption phase for the additives (e.g., organic matter).

3.2. Effects of the Presence of Organic Matter in a Sample. For hydrophobic nonionized chemical additives, the mass sorbing or sorbed to organic matter may represent a substantial proportion of the total mass of the additive in a sample, whether this sample is the suspended matter collected from surface waters, wastewater treatment plant effluent, beach sand, seabed sediment, or soil. Simulations given in Figure 2 show that the fraction of the chemical additive present and incorporated into plastic ($N_{P\text{-}CAD}/N_{S\text{-}CAD}$) varies with the ratio of OC to additive loaded plastic content from 1 to 1000 mg μg^{-1}. The units of the x-axis of Figure 2 translate for hypothetical dry sediment with a 5% OC content to an additive-loaded plastic content decreasing from 50 to 0.05 μg g^{-1} of the sediment. In these simulations, a $C_{CAD\text{-}free}$ of 1 ng L^{-1} combined with a log K_{OC} and log K_{pw} of 4, 5, and 6 (with $K_{pw} = K_{OC}$ for simplicity) simulated fractions sorbed to OC and the plastic contained in the sample. These simulations show that in these conditions, the presence of OC in the sample should reach an m_{OC}/m_{Px} ratio of >1000 mg μg^{-1} for OC sorption to become substantial for an additive with log K_{pw}

or log K_{OC} of 4. In other words, m_{Px} needs to be >0.05 μg in 1 g of our hypothetical sediment for the $N_{P\text{-}CAD} \sim N_{S\text{-}CAD}$. For the same $C_{CAD\text{-}free}$, this m_{Px} value will needs to be >5 μg per g of sediment for an additive with log $K_{pw}/K_{OC} = 6$. At an m_{Px} of 0.05 μg ($m_{OC}/m_{Px} = 1000$ on Figure 2), most of the additives present in the sample would be sorbed to the organic matter.

These simulations estimate an additive's phase distribution or speciation when the OC and plastic content are known. Significantly, these simulations can also indicate whether a phase separation is needed before the chemical extraction of the additive. Notably, this modeling can also be performed at the posterior to evaluate this phase distribution. We take a concrete example from the literature. La Nasa et al. measured the content of plasticizers in beach sand likely containing microplastics.[28] Dibutyl phthalate in core sand was measured at a concentration of 1057 and 1571 ng g^{-1} sand (different depths). Simulations assuming log K_{OC} = log K_{ow} = 4.7 (from PubChem) for dibutyl phthalate, a $C_{CAD\text{-}free}$ = 0.1 ng L^{-1}, and a fraction of OC in beach sand (f_{OC}) of 0.1% were performed, resulting in estimates of total dibutyl phthalate concentration in the sand of 6 orders of magnitude below the observed concentrations.

Our modeling demonstrated that the plasticizer is most likely an additive to plastic in this real example. On the other hand, if this plasticizer was present as an original additive in microplastic particles at a 5% level, this would be equivalent to 21 and 31 μg of dibutyl phthalate-loaded plastic per g of sand. This seems to be more realistic.

In the next set of simulations (Figure S1), instead of varying the hydrophobic/partitioning properties of the additive, we changed the fraction of additive-loaded plastic in the sample. The simulations refer to an additive with log K_{pw} or log K_{OC} = 5 loaded at 5% level in the plastic and the proportion of plastic x, P_{px} = 0.001. The $C_{CAD\text{-}free}$ was set to 1 ng L^{-1}. Under these conditions, the f_{Px} needs to be >0.00001 for a substantial proportion of the additive in the sample to be present as an additive to the plastic. Sorption to OC becomes substantial for an m_{OC}/m_{Px} between 1000 and 10 000 mg μg^{-1}. Below that m_{OC}/m_{Px} threshold, under a low f_{Px}, a significant part of the additive is sorbed to the plastic. This is exemplified in the series of 3-phase distribution graphics of Figure S2. However, in that specific case, a relatively high proportion of plastic was used (8%). Such a proportion of plastic could result from a particular separation step, such as density separation. It should be emphasized that when the amounts of certain plastics (and OC) have been determined in a sample, the modeling presented herein allows estimating (i) whether detecting plastic-loaded additives is realistic and (ii) minimum sample size for extraction to ensure that the additive concentrations are above the LOD. This may have implications in designing a sampling procedure and sample processing methods for microplastics in various environmental matrices.

3.3. Chemical Additive Versus Sorbing Chemical: Benchmarking.

Another way to gain information on the speciation of a chemical is to compare the partitioning of chemical additives with that of other chemicals with similar hydrophobicity/partitioning properties but not used as additives. Comparing the observed particulate phase to freely dissolved distribution coefficients can help reveal a significant contribution of additive-loaded plastics to the overall particulate phase concentration. When the additive in the plastic does not contribute to exchange with the freely dissolved phase, this could result in discrepancies in apparent

K_d in soils and sediments, in a way similar to black carbon.[31] In Figure S3, we simulated benchmarking with a chemical with log K_{ow} = 5 (and $K_{OC} = K_{pw} = K_{ow}$) and $C_{CAD\text{-}free}$ = 0.1 ng L^{-1}. The additive had a higher hydrophobicity (log K_{ow} = 6) and a $C_{CAD\text{-}free}$ 30% of that of the benchmarking chemical. At equilibrium, a ratio of the concentration of the additive over that of the reference chemical of 3 can be expected for the particulate phase, when sorption to OC is the main driver of distribution. For Figure 3, we used C_{OC} values representing the
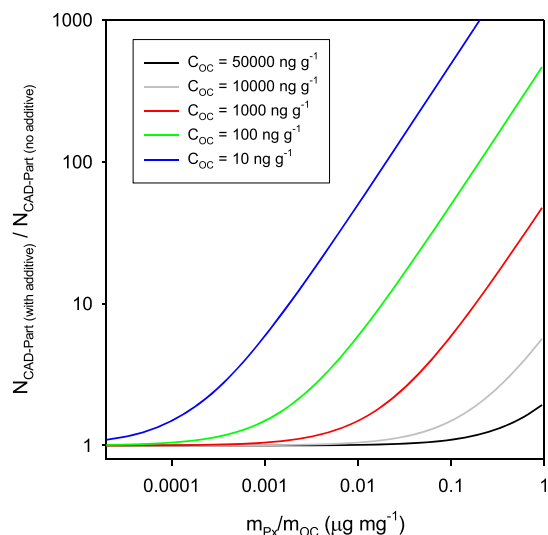

Figure 3. Simulated relative increase in the total additive amount in particulate matter (plastic and OC) in the presence of the CAD as additive. This relative increase is plotted for various C_{OC} (ng g^{-1} OC; $K_{OC} \times C_{CAD\text{-}free}$). For this simulation, the log K_{pw} and K_{OC} for the CAD were set to 6, the proportion of plastic in the sample to 2% of the OC content, and the proportion of CAD in plastic x = 5%.

range of concentrations that could be found for flame retardants such as PBDEs in coastal sediments[32] or other additives in sediments or sewage sludge (Table S1). An increase in the content of additive-loaded plastic (5%) affects this ratio substantially. In these conditions, an order of magnitude increase in the ratio can be expected for an additive-loaded plastic content above 10 μg per mg of OC. Intuitively, it can be expected that the environmental levels (not related to the additive-loaded plastic content) affect the threshold at which such differences can be observed. The lower the $C_{CAD\text{-}free}$, the lower the OC-sorbed concentration (C_{OC}) and the more sensitive the phase distribution of the additive to the presence of additive-loaded plastic is. This is shown in Figure 3, where the relative increase in the particulate concentration of the additive is shown as a function of the proportion of the additive-loaded plastic in the sample and as a function of the OC-sorbed concentrations. Because C_{OC} is the product of K_{OC} and $C_{CAD\text{-}free}$, this is also equivalent to modifying $C_{CAD\text{-}free}$ or assessing the distribution of additives with different hydrophobicities (K_{OC}). It shows that the lower the $C_{CAD\text{-}free}$ or, the lower the hydrophobicity, the more likely it is for additive-loaded plastic particles to impact apparent additive distribution in a sample. The presence of 1 μg of additive-loaded plastic does not influence the particulate phase concentration to any extent for a C_{OC} of 50 000 ng g^{-1}. However, an m_{Px}/m_{OC} level of as low as 0.01 μg mg^{-1} substantially increases the additive concentration in the particulate phase for C_{OC} of 10−100 ng g^{-1}. The possible dissipation of the additive during the aging of
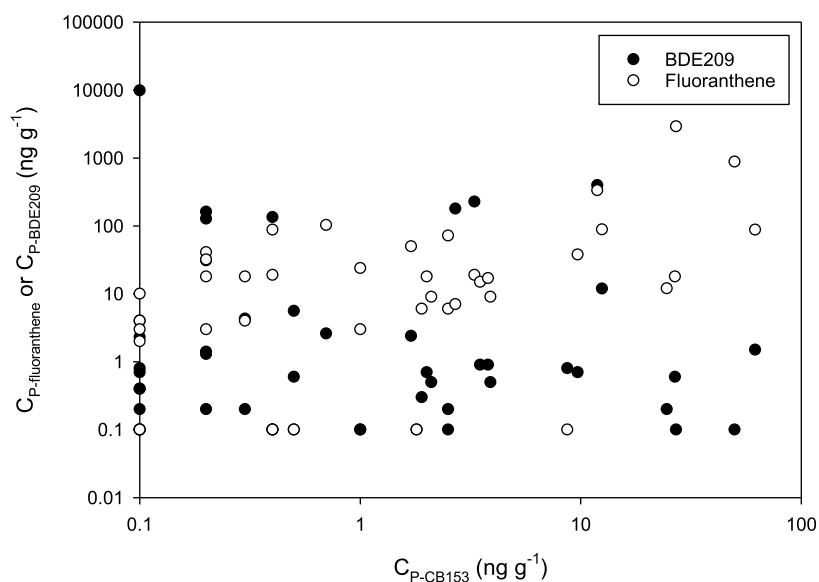
Figure 4. Concentration of the flame retardant BDE209 and the polycyclic aromatic hydrocarbon fluoranthene in plastic fragments from the open ocean, remote, and urban beaches with the concentration of the polychlorinated biphenyl CB153. Data are from (Hirai et al., 2011).

the plastic has the opposite effect and tends to lower the impact of the plastic phase on the distribution.

To put the proposed modeling approach into context, we attempted to benchmark the concentration of the flame retardant BDE209 and the PAH fluoranthene with the concentration of CB153 (Figure 4), measured by Hirai et al. (2011) along with various organic contaminants in plastic fragments from the open ocean and remote and urban beaches.[33] This benchmarking shows that BDE209 is likely to be present as an additive for seven plastic fragments rather than having sorbed to the plastic fragments. While BDE209 can potentially be an additive to the plastic fragments, this is not the case for CB153 and fluoranthene. It is worth noting for this data set that fluoranthene concentrations observed in plastic debris (1–1000 ng g^{-1} plastic) are consistent with realistic values for log K_{pw} of 4–5 and freely dissolved fluoranthene concentrations of 0.1–10 ng L^{-1} in waters of marine environments in case of equilibrium distribution between water and plastic.[34,35]

Many procedures and techniques are available to evaluate this speciation. Passive sampling can be applied to water, sediment, and sludge to determine $C_{CAD\text{-free}}$ or polymer concentration at equilibrium with the water phase.[16] A passive sampling approach can also complement the exhaustive extraction of solid samples containing microplastics by measuring an accessible concentration of the labile fraction sorbed to organic matter.[36,37] The difference in concentration between the two may result from an additive in the microplastic unable to desorb/dissipate easily from the plastic. Whether micro- or nanoplastic particles present in a sample or in the environment sorb to the surface of polymeric passive samplers is yet to be verified.

3.4. Influence of Additive Dissipation on Speciation. Another factor not to be underestimated is the potential release of an additive from plastic during its life once released into the environment. We have previously used a model to calculate the proportion of a chemical dissipating from a microplastic particle over time when the additive diffusion coefficient in the plastic and particle size is known.[4] Because in this model, mass transfer is solely the result of diffusion within

the plastic and limited by transfer from the plastic into the outer environment, it represents a worst-case scenario or maximum expected dissipation of a chemical additive. Additive diffusion coefficients are a function of the additive itself, the type of plastic, and other components in the plastic. Generally, higher diffusion coefficients are found for plastics with glass transition temperatures (T_g) below the ambient temperature or for plastics with a low level of crystallinity. This is the case for polyethylene with T_g of −125 or 130 °C. Additives tend to have lower diffusion coefficients in polypropylene (isotactic), polystyrene, or polyvinyl chloride because T_g values for these plastics are over 60 °C. We listed reported measured values of diffusion coefficients for selected additives in plastics or plastic fragments and particles in Table S2.

Figure S4 presents simulations of the maximum proportion of a chemical additive dissipated from a microplastic particle for a given time, particle size, and additive diffusion coefficient. The dissipation times span from 0.5 days, which may be representative of manipulation time in the laboratory, batch extraction, or grinding procedures, to 10 days or 1 or 10 years representative of the potential particle residence time in a sewage system, or presence and transport to the aquatic environment (not accounting for particle break-down through other processes). At first glance, these simulations show that microplastic particle size (diameter in this case) and dissipation time significantly impact the proportion of additives that can legitimately dissipate from MPs. For example, an additive with a log $D = -16$ m^2 s^{-1} in a specific microplastic particle has the potential to dissipate completely from particles with a diameter of 0.1 and 1 μm during a dissipation time of 0.5 d, while it mostly remains in microplastics with a diameter of 0.1 and 1 mm in that same period (Figure S4). For the same additive–plastic combination, a dissipation time of 10 y is needed to see a substantial release of the additive from a particle with a 1 mm diameter, unless other processes such as UV degradation or erosion accelerate the release process. According to Figure S4, a negligible loss of additives in microplastics may be expected for additive–plastic combinations with log $D < -22$ m^2 s^{-1}, for microplastic diameters down to 100 nm and dissipation times of up to 10 y. This

threshold is in the range of diffusion coefficients reported for brominated flame retardants in acrylonitrile butadiene styrene polymers (Table S2).[19] Diffusion coefficients (log D at 10 °C) for flame retardants such as BDE209 or BTBPE used as the rear cover of cathode ray tube and liquid crystal display computer monitors were in the range of −27.51 to −24.0 m^2 s^{-1} and are below this threshold. This means that this additive−plastic combination results in an additive that does not dissipate to any significant extent in the aforementioned time scale. Other additive−plastic combinations are likely to result in near-complete dissipation of the additive under relevant timescales. As shown in Table S2, this is the case for UV filters or plasticizers with substantially higher measured diffusion coefficients in polypropylene.[38] It is worth noting that for an additive loaded at 5% in weight in plastic, a 99% dissipation would nonetheless result in a remaining additive concentration in the plastic of 500 ng mg^{-1} of plastic.

Although not the focus of this study, certain factors such as additive characteristics like K_{pw},[18] log D, MNP particle size (diameter), and dissipation time can be combined and compiled to identify and prioritize additives that dissipate or are unlikely to dissipate from MPs released into the environment and cause a risk, for example, to biota ingesting such particles. Physicochemical characteristics of the plastic−additive combinations, together with parameters such as particle size or processes such as photodegradation of microplastics, will either promote enhanced (bio)availability of the additive or lower lability and increase the potential for transport over long distances in the environment.

3.5. Accuracy of the Model Parameters. Such modeling can result in clear-cut situations, while in some cases, characterization of additive speciation may be challenging. As for any modeling exercise, it is also useful to consider the uncertainties associated with selecting values for model parameters (e.g., physicochemical properties of the chemical), the model assumptions, and the empirical data. In our modeling applications, the possible implications of a plastic-associated additive fraction are identified through an internal consistency check. The input of empirical values into our modeling framework results, for example, in the estimation of a log K_{OC} that can then be compared with log K_{ow} or literature values to establish whether the value is realistic or if the plastic-associated additive contributes to the observed distribution coefficient. The conclusion of this internal consistency check can be a clear-cut situation with the observed log K_{OC} exceeding log K_{ow} significantly. In other cases, when the proportion of plastic (relative to organic matter) in a sample is low, the data set remains in a gray area where it is impossible to draw solid conclusions.

Estimates of organic matter or carbon content and microplastic content can be subject to some uncertainty. The development of pyrolysis-GC/MS methods in the near future will lower the uncertainty in plastic content estimates.[39] The type of organic carbon and the presence of black carbon can affect additive partitioning. Therefore, it may be judicious to estimate the proportion of black carbon in organic matter. When considering additive extraction and analysis, working far away from the limits of quantification helps reduce uncertainties, particularly when working with plastic additives for which contamination cannot be avoided during sample work-up in the laboratory (e.g., phthalates). In that case, the procedural blank is very crucial.

Additive dissipation from MNPs contributes to reducing C_{CADx}. This means that it is possible that for a sample with aged plastics, the additive-loaded plastic content may have lost a substantial amount of additive, and it would be difficult to sample a sufficient amount of plastic to identify this fraction. In addition, during nonexhaustive extractions, additives can dissipate from sorbed to organic matter or adsorbed to microplastics. This may be confounded by plastic-associated additives able to dissipate from microplastics. Comparison of organic carbon or plastic-associated additive concentrations with those measured freely with published values of log K_{pw} or log K_{OC} relies on the assumption that concentrations are at equilibrium. This is not always the case. Plastic aging may also impact sorption parameters, particularly in the case of adsorption. A generic K_{pw} has been used in this modeling. However, additive distribution between water and plastics may be more complex than such a value. Using log K_{OC} = log K_{ow} as an estimate of sorption to organic matter may underestimate sorption in the presence of black carbon. Increased sorption depends on the additive's affinity for black carbon and the proportion of black carbon. This is particularly relevant for samples from urban environments.

4. CONCLUSIONS

The modeling presented herein can be used to design the sampling and analysis techniques for microplastic-associated additives based on the speciation of the additive in an environmental matrix being sampled. Before sampling, this can be done to estimate the minimum sample size or masses of microplastics to exceed the detection limits of instrumental analysis or post-sampling to distinguish between sorbed additives and those added during plastic production. Limited quantitative information is available for additives used in the production of plastics compared to the sorbed additives.[40] This indicates a need for more studies on the quantification of chemical additives related to plastics production, for example, brominated flame retardants, such as hexabromocyclodode-canes, used in polystyrene foam.[41]

Some sample processing before extraction and analysis may be required, particularly when other matrix components such as organic matter represent a major sorption phase for additives. For example, the characteristics of wastewater treatment plant effluents in terms of both solids and organics content may vary significantly between wastewater treatment plants employing different treatment processes such as conventional activated sludge and membrane bioreactor.[42] In some cases, sample processing may focus on separating the microplastics from the matrix (e.g., in soils or sediments) or eliminating the matrix (e.g., with KOH or H$_2$O$_2$). In an attempt to distinguish between additives sorbed to the matrix and the plastics from those initially present in the plastics, nonexhaustive, or mild extractions, as developed to estimate accessible concentrations of organic contaminants in soils and sediments with passive samplers or to evaluate desorption rates, can be applied to the samples before a more exhaustive extraction such as Soxhlet or pyrolysis-GC/MS. This procedure will remove the labile or easily desorbable concentration of additives but will not extract microplastic-associated additives. It is worth noting that, among others, the wastewater characteristics may affect the amount of additives sorbed on microplastics. Future research on the effect of the matrix and other parameters (e.g., pH and temperature) on the sorption of additives on microplastics is needed to get insights

into this. The modeling reported herein estimates the expected speciation of an additive between organic matter/carbon, microplastics, and free form. When sampling an aquatic matrix such as surface waters and wastewaters, or solid matrices such as sediment, sludge, and soils, a passive sampling measurement can be undertaken to estimate a freely dissolved concentration, $C_{CAD-free}$, that can, in turn, be used to help clarify our understanding of additive speciation in an environmental sample/compartment. This is possible for nonpolar and nonionized additives for which polymer—water partition coefficients, for the polymer used in passive sampling are known. Instead of $C_{CAD-free}$, an additive concentration in the polymer (e.g., LDPE or silicone rubber) at equilibrium with the water can be calculated. It can be compared with the levels in the microplastic/matrix. Lastly, it is relatively straightforward to analyze for additives of interest and other widespread compounds with similar properties but not used as additives. Benchmarking with these compounds, combined with passive sampling, can also help distinguish sorbing additives from those associated with microplastics. The relative proportions of OC and microplastics in the sample are crucial factors influencing our ability to undertake this benchmarking.

Another relevant factor to consider in the speciation of microplastic-associated additives is the diffusion coefficients of the additives in the plastic and overall dissipation from particles during their lifetime. The ability of relevant additives to diffuse and move out of the particles will partly affect whether microplastic-associated concentrations are likely to remain significantly higher than those achieved through sorption only. In the future, thresholds for particle size and diffusion coefficient combination may be established to categorize additive bioavailability and their potential to dissipate from microplastics.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsestwater.1c00310.

> Concentrations of relevant additives in matrices such as sediment and sewage sludge or effluent; description and selected physicochemical properties of relevant plastic additives, including reported diffusion coefficients in plastic; simulations of additive distribution with two different scenarios; simulations of benchmark of additive concentrations with a similar type of chemical not used as a plastic additive; and simulations of the proportion of additive dissipation as a function of the particle size and diffusion in the polymer (PDF)

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Notes

The authors declare no competing financial interest.

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