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Effect of Mass Fraction on Leaching Kinetics of Hydrophobic Ultraviolet Stabilizers in Low-Density Polyethylene

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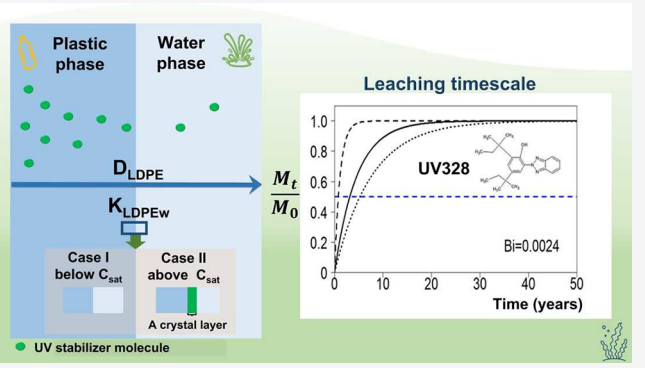
ABSTRACT: The leaching kinetics of five hydrophobic ultraviolet (UV) stabilizers from low-density polyethylene (LDPE) (micro)-fibers into water was evaluated in this study, with variation of the mass fraction (ω = 0.1−2.0 wt %) of the stabilizers. A one-dimensional convection−diffusion model for a cylindrical geometry, requiring partitioning between the LDPE fibers and water (K_{LDPEw}) and the internal diffusion coefficients (D_{LDPE}), was used to evaluate the leaching process and the leaching half-life of the target UV stabilizers at ω < 0.5 wt % (Case I). Diffusion through the aqueous boundary layer is the rate-determining step, and the leaching half-life is predicted to be very long (a few months to years) under unaffected conditions. When the UV stabilizers are supersaturated within LDPE fibers (i.e., ω > 0.5 wt %, Case II), the possible formation of a surficial crystal layer of the additives on the LDPE fiber extends the time scale for leaching compared to that in Case I due to the requirement of overcoming the crystallization energy. This study provides a fundamental understanding of the leaching profiles of plastic additives for assessing their potential chemical risks in aquatic environments; further studies under the relevant environmental conditions are required.



KEYWORDS: *microplastics, UV stabilizers, mass fractions, leaching kinetics, partition coefficients, diffusion coefficients, aquatic environment*

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INTRODUCTION

Plastic pollution has become an urgent global issue due to its widespread occurrence and persistence in the aquatic environment. Plastic production has increased consistently since the 1950s[1−3] because of its versatile properties.[4,5] Microplastics (MPs), which are defined from their size as having a length of less than 5 mm (although multiple dimensions are preferred in the definition of microfiber),[6] have been raising concerns as an unignorable part of plastic pollution.[7] MPs are a source of harmful plastic additives (flame retardants, plasticizers, UV stabilizers, antioxidants, and pigments[8−10]), which are added at different mass fractions, are not covalently bonded to the plastic matrices, and thus have potential ecological impacts.[11] Additives are leached from the plastic phase into the aquatic environment, driven by the fugacity gradient between the two media[11] explained by diffusion within the plastic phase, partitioning at the plastic−water interface, and mass transfer through the water boundary layer. Depending on the chemical, plastic, and properties of the adjacent medium, the leaching of additives from (micro)plastics is dominated by the diffusion rate in the plastic phase or aqueous boundary layer.[12] In real environments where the leaching is far from phase equilibrium, the leaching kinetics is the most important process to understand how fast additives are liberated from MPs.[13]

The leaching kinetics of plastic additives have been investigated using several mathematical desorption models for different geometries.[10,14−18] A diffusion model for hydrophobic organic chemicals (HOCs) revealed that diffusion within homogeneous high-density polyethylene (HDPE) and polyvinyl chloride (PVC) spheres was the rate-limiting step of leaching, and the leaching half-lives ranged from HOCs of 10 days to a few years for spherical pellets (1 mm radius) depending on the degree of crystallinity.[10] The desorption data for spherical marine pellets (2 mm radius) was described by the aqueous boundary layer (ABL) model showing the leaching time scale from a few days up to a thousand years, depending on the stirring conditions and hydrophobicity of polychlorinated biphenyls (PCBs).[14] Lee et al. explained the desorption of hexachlorocyclohexanes (HCHs) and chlorinated benzenes (CBs) from PE and polypropylene (PP) using a prediction model employing the mass transfer Biot number.

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Diffusion within the PE/PP films (for HCHs, the *n*-octanol/water partition constant, log $K_{ow} \approx 3-4$) and external mass transfer (for CBs, log $K_{ow} > 5$) across the aqueous boundary layer in seawater is documented.[15] Leaching of brominated flame retardants (BFRs) from a spherical pellet to water/fish oil/gut fluid was controlled by diffusion in the plastic;[16−18] the estimated time scale for leaching BFRs into water was up to billions of years.[16] The estimated time for leaching hydrophobic phthalates from spherical PVC MPs was over 1,000 years, controlled by mass transfer through the ABL.[19] Generally, diffusion within the plastic phase usually controls the rate for less hydrophobic compounds (log $K_{ow} < 4$),[10,15] while mass transfer through the ABL is the rate-limiting step for HOCs with log $K_{ow} > 4$.[14,15,19] Dissolved organic matter in water can facilitate chemical transfer by reducing mass transfer resistance in the ABL,[14] leading to diffusion within the plastic becoming the rate-controlling step.[17,18] Nevertheless, leaching studies focusing on organic plastic additives are still limited, and most leaching mechanisms were described for sheets or spherical particles, whereas (micro)plastics generally occur as fibers in the aquatic environment.[20,21] Moreover, the mass percentage of plastic additives is highly variable. According to classical polymer theories, additives can be completely mixed with polymer segments. However, the additives may form a separate phase if their mass fraction in the polymer exceeds a certain point.[12,22] Thus, the mass fraction can affect the leaching of plastic additives, particularly when hydrophobic compounds are present at high mass fractions, where a crystal layer covers the polymer surface and the removal of the layer in water would take a long time. Therefore, the leaching kinetics may depend on the mass fraction of the additives, size, and geometry of the MPs.

UV stabilizers, common organic additives typified by benzophenones and benzotriazoles, prevent photodegradation and prolong the lifespan of plastics.[23,24] They are environmentally persistent aromatic molecules that are highly hydrophobic and have low volatility.[25] Benzotriazole UV stabilizers, namely 2-(2*H*-benzotriazol-2-yl)-4,6-bis(2-methyl-2-butanyl)phenol (UV328), have been listed as Persistent Organic Pollutants under the Stockholm Convention,[26] 2,4-di-*tert*-butyl-6-(5-chloro-2*H*-benzotriazol-2-yl)phenol (UV327) is currently classified as a substance of very high concern under the EU legislation REACH,[27] and (2-hydroxy-4-octoxyphenyl)phenylmethanone (UV531) has been listed under the European Community Rolling Action Plan for evaluation in upcoming years.[28] Some UV stabilizers (such as 2-(5-chloro-2*H*-benzotriazol-2-yl)-4-methyl-6-(2-methyl-2-propanyl)phenol (UV326), 2-(2*H*-benzotriazol-2-yl)-4-(1,1,3,3- tetramethylbutyl)phenol (UV329), and (2-hydroxy-4-octoxyphenyl)phenylmethanone (UV531) are currently listed as high production volume chemicals by the Organization for Economic Co-operation and Development (OECD).[29] Many organic UV stabilizers have been detected in many environmental matrices worldwide, such as rivers,[24] seawater,[30,31] sediments,[32] biota,[23,33] and human tissue.[34] UV stabilizers have documented adverse effects (potential endocrine disruption, metabolic imbalance, and carcinogenicity).[35,36] However, their fate and transport in the aquatic environment and mechanisms of leaching from plastic matrices into aquatic environments are ill-defined.[37] To assess the potential chemical risks and contamination of aquatic environments, the kinetics of leaching UV stabilizers from MPs must be understood because MPs are suspected as persistent sources for hydrophobic plastic additives such as UV stabilizers.

Herein, the effects of the mass fraction (ω) of five hydrophobic UV stabilizers in LDPE on the leaching kinetics in aquatic environments is evaluated. LDPE was chosen as the model plastic material because phase equilibrium of UV stabilizers between LDPE and water has been well studied[22] and PE is the one of most abundant MP materials in the aquatic environment.[4] The variation of partition coefficients between LDPE and water (K_{LDPEw}) with different mass fractions and the diffusion coefficients in LDPE (D_{LDPE}) of the five UV stabilizers are experimentally determined as key parameters by using a leaching model characterized by the mass transfer Biot number. The leaching of UV stabilizers from LDPE fibers into water is predicted by applying a one-dimensional convection-diffusion model for a cylindrical geometry. The fractions of plastic additives leached from the MPs, measured in a batch test, are compared to the model-predicted values. The leaching profiles of the five selected UV stabilizers facilitate fundamental understanding of the leaching of UV stabilizers and, consequently, the ecological risks associated with MPs in the aquatic environment.

MATERIALS AND METHODS

Chemicals and Materials. All reagents were purchased from Sigma-Aldrich (St. Louis, MO, USA). The five selected UV stabilizers included four benzotriazole UV stabilizers, UV 326 (>98%), UV 327 (>98%), UV 328 (>98%), and UV 329 (>98%), and a widely used benzophenone-type photostabilizer, UV 531 (>98%). HPLC-grade organic solvents (methanol, *n*-hexane, and acetonitrile (ACN)) were used. Detailed information regarding the five UV stabilizers is provided in Table S1. LDPE fibers (radius ∼75 μm; length ∼5 mm) containing the desired mass fractions (i.e., 0.1, 0.2, 0.5, 1.0, 2.0 wt %) of the selected UV stabilizers were manufactured using a benchtop extruder (LME, Dynisco Inc., Franklin, MA, USA), as described elsewhere.[22] The LDPE films (thickness = 75 μm; density = 0.94 g cm^{-3}) were used to determine the D_{LDPE} of the UV stabilizers in the LDPE fibers. Medical-grade polydimethylsiloxane (PDMS) sheets (thickness = 1 mm; density = 1,170 kg m^{-3}) were employed in the batch leaching kinetics experiments and determination of partitioning between the LDPE fibers and water. Additional information on the LDPE films and PDMS sheets can be found in the Supporting Information, Section S1.

Surface Characterization and Identification of Crystalline Phase. *Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Spectroscopy (EDS).* LDPE fibers with the five UV stabilizers at different ω were fixed on an aluminum sample tray, and the surfaces were coated with platinum. Field-emission scanning electron microscopy (FE-SEM-QUANTA 250 FEG, FEI Co.) measurements were performed at different positions at an acceleration voltage of 10 keV. The surface of the plastic fiber was chemically characterized through quantitative analysis via energy dispersive spectroscopy (EDS) using the SEM/EDS system.

Fourier-Transform Infrared (FTIR) Spectroscopy. The surface of the LDPE fibers was characterized by using an FTIR spectrometer (Nicolet iN 10MX, Thermo Fisher Scientific, Waltham, MA, USA) by averaging 32 scans in the spectral range of 4000−650 cm^{-1}, with a resolution of 4 cm^{-1}, in transmission mode.

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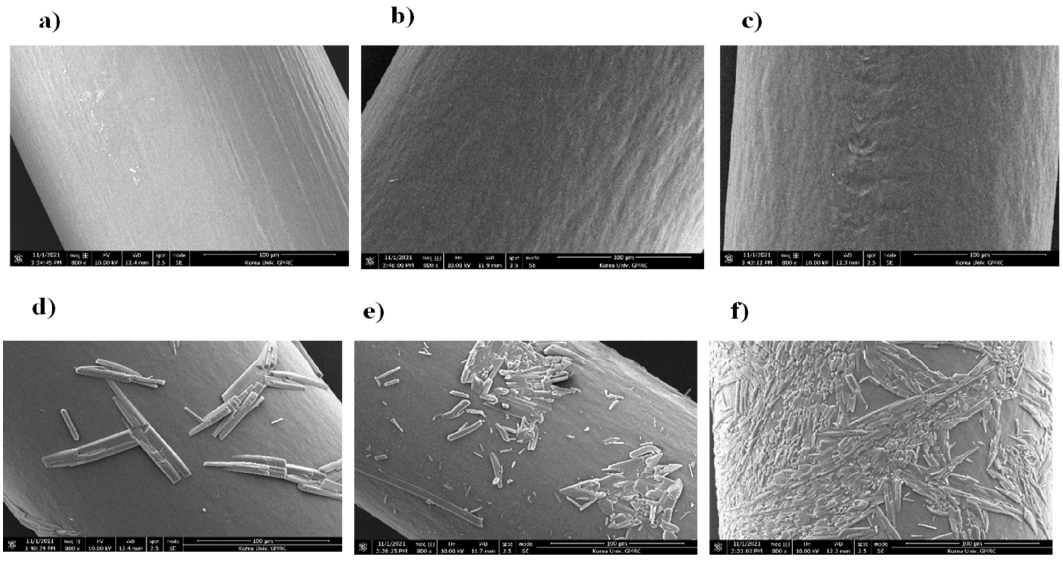

Figure 1. SEM images of LDPE fiber containing (a) 0, (b) 0.1, (c) 0.2, (d) 0.5, (e) 1.0, and (f) 2.0 wt % of UV326.

X-ray Diffraction (XRD). The degree of crystallinity of the pristine LDPE and LDPE fibers containing 0.1 and 2.0 wt % of UV 326 was evaluated by X-ray diffraction (SmartLab, Rigaku, Japan). Further details are given in Supporting Information, Section S2.

Partitioning between Plastic and Water (K_{LDPEw}). The K_{LDPEw} values were obtained using third-phase partitioning[38] owing to the very low water solubility of the five hydrophobic UV stabilizers[22] and long equilibration time.[39] Based on the thermodynamic cycle, K_{LDPEw} was estimated using the following partitioning equation

$$K_{LDPEw} = \frac{K_{LDPEsm}}{K_{PDMSsm}} K_{PDMSw} \quad (1)$$

where K_{LDPEsm} is the partition coefficient of the UV stabilizer between the LDPE fiber and ACN/water mixture (4:6, v/v), K_{PDMSsm} is the partition coefficient of the UV stabilizer between PDMS and the ACN/water mixture (4:6, v/v), and K_{PDMSw} is the partition coefficient between PDMS and water, measured using the ABL permeation method.[25] The experiments and methods to determine K_{LDPEsm} and K_{PDMSsm} are provided in the Supporting Information, Section S3.

Internal Diffusion Coefficients of Plastic Additives. The diffusion coefficients of the UV stabilizers in the plastic materials were determined using the film-stacking method,[15,40] in which the polymer used should be homogeneous and the applied pressure has no effect on the diffusivity in the polymer (i.e., LDPE), which is recommended to obtain experimental internal diffusion coefficients for a wide range of organic compounds.[41] The diffusion coefficients of the UV stabilizers in the plastic films were estimated by using Fick's second law of diffusion in one dimension. The best-fit value of D was obtained using the nonlinear least-squares (nls) function in R version 4.2.0 (R Development Core Team, 2022). Detailed information regarding this process is provided in the Supporting Information, Section S4.

Evaluation of Desorption Kinetics. In our previous study, the equilibrium concentration of the tested UV stabilizers increased linearly with mass fraction up to 0.5 wt % in LDPE (except for UV531), suggesting the loss of UV stabilizers from LDPE by leaching to the contacting medium and/or by phase separation on the polymer surface due to unfavorable interaction with the PE polymer.[22] Therefore, leaching of the UV stabilizers from the LDPE fibers with ω = 0.1, 0.2, 0.5, 1.0, and 2.0 wt % was examined in batch experiments using two solutions: 10 mL ACN/water (4:6, v/v) for proof-of-principle and water. The details of the experiment are given in the Supporting Information, Section S5. The concentrations of the additives in the water, PDMS, and LDPE fibers were analyzed using LC-MS/MS (details in Section S7, and the mass spectrometry detection parameters are listed in Table S2).

Leaching Model. A 1D convection−diffusion desorption model was used to simulate leaching of the UV stabilizers from the plastic fibers into ACN/water (4:6, v/v) or water. The model is explained in detail in the Supporting Information, Section S6.

RESULTS AND DISCUSSION

Surface Characterization and Crystallinity of LDPE Fibers. The surface morphologies of the LDPE fibers containing the UV stabilizers at different mass fractions (ω = 0.1−2 wt %) were analyzed using SEM and FTIR. A layer of precipitates on the surface was observed in the SEM images of the LDPE fibers containing UV326, UV327, UV328, and UV329 at ω > 0.5 wt %, whereas the fibers with ω = 0.1−0.5 wt % exhibited smooth and featureless surfaces, similar to that of the LDPE fibers without the UV stabilizers (Figures 1 and S1−4 in the SI). Notably, the amount of precipitate on the surface of the plastic fibers increased as ω increased. This is consistent with the XRD results, in which the degree of crystallinity increased owing to the fiber-forming process and the addition of UV326 (Table S4 and Figure S6 (SI)). The surface of the LDPE fibers remained smooth with up to 1.0 wt % UV531, and a small amount of UV531 crystals was observed on the surface of the fibers with 2.0 wt % UV531. EDS was used to chemically characterize the surfaces of the plastic fibers (Table S3 and SI). The chlorine content increased with increasing ω values for the LDPE fibers with UV326 and UV327 (Table S3). The concentrations of oxygen and nitrogen also increased with increasing mass fraction for the fibers with UV328 and UV329. For the fibers containing UV531, the

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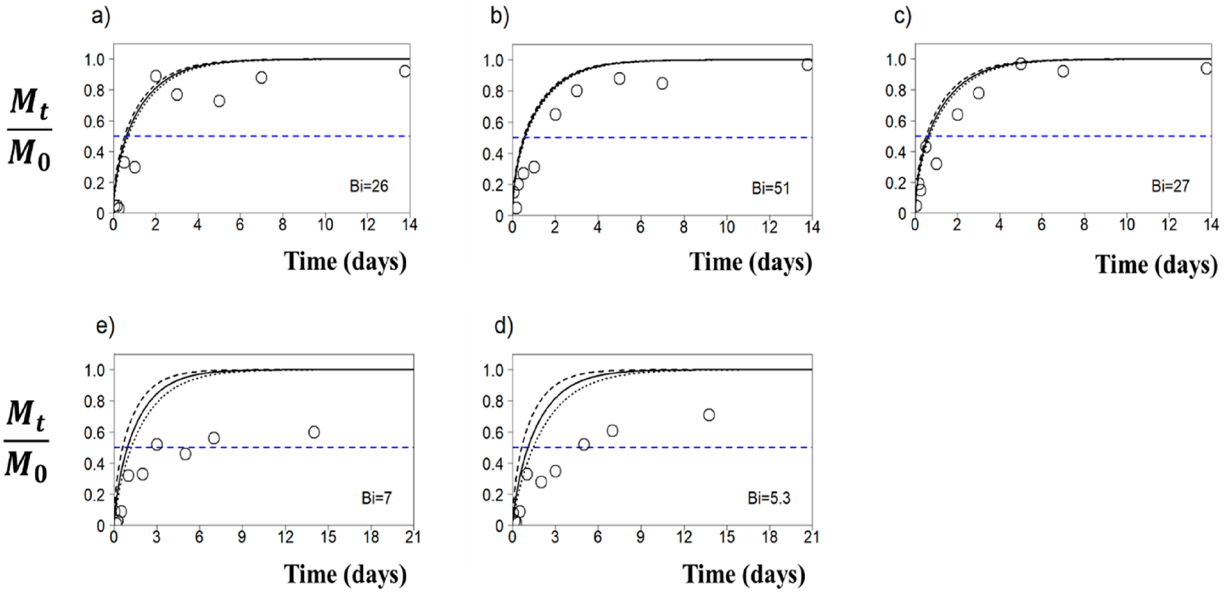

Figure 2. Fraction of UV328 leached (M_t/M_0) from LDPE fibers into ACN/water (4:6, v/v) at desorption time t for ω = (a) 0.1, (b) 0.2, (c) 0.5, (d) 1.0, and (e) 2.0 wt %. Comparison of experimental data (empty circles) for UV328 in plastic fibers. Line values were predicted using eq S4, where the thickness of the aqueous boundary layer (δ_w) is 10 μm (dashed lines), 50 μm (solid lines), and 100 μm (dotted lines). Biot numbers were calculated at δ_w = 50 μm; the blue dashed line indicates the half-leaching amount of the UV stabilizers.

difference in the amount of oxygen with the variation of mass fraction was not significant.

The surfaces of the LDPE fibers were further characterized by FTIR spectroscopy. More IR transmission peaks were observed at 700−1500 cm^{-1} in the spectra of the LDPE fibers with ω = 1−2 wt % (Figure S5) compared to those of the fibers with ω = 0.1−0.5 wt % and that of the pristine LDPE fibers. Interestingly, the LDPE fibers with UV531 exhibited generally similar patterns over the entire ω range (0.1−2 wt %), both with and without UV531, consistent with our previous findings.[22] The solubility of UV stabilizers in a polymer depends on the size disparity between the UV stabilizers and polymer molecules and their compatibility.[22,42] Thus, mixing is generally not favorable in the plastic phase due to the net repulsive intermolecular forces between the UV stabilizers and LDPE (except UV531) at ambient temperature. "Blooming" may occur with the precipitation of the four benzotriazoles on the surface of the LDPE fibers at high ω (1.0 and 2.0 wt %), as shown in SEM images. Differences in the surface morphology and degree of crystallinity of the LDPE fibers with variation of ω for the five selected UV stabilizers might influence the kinetic mechanisms of leaching into water due to the extremely low solubility of these UV stabilizers in aqueous media, as explained hereinafter.

Determination of Partition Coefficients between LDPE Fiber and Water (K_{LDPEw}). Reliable data for the partitioning of plastic additives between plastic and water are required to evaluate the leaching kinetics.[43] However, the use of experimental partitioning values to obtain the leaching profile of HOCs is limited.[15] Figure S7 (SI) shows good linear relationships between the concentration of the target chemicals in PDMS (C_{PDMS}) and the ACN/water (4:6, v/v) mixture (C_{sm}) within the evaluated concentration range (R^2 > 0.94). Table S5 presents log K_{PDMSsm}, K_{LDPEsm}, K_{PDMSw}, and K_{LDPEw} for the five UV stabilizers at 0.1−2.0 wt %. The mass fraction in the range of 0.1−0.5 wt % did not influence the log K_{LDPEw} values significantly for all selected UV stabilizers (except UV 531). The log K_{LDPEw} values were significantly greater at 1.0 and 2.0 wt % due to the layer of UV stabilizer crystals on the surface of the LDPE fibers. The calculated log K_{LDPEw} values for benzotriazoles at 0.1−0.5 wt % and benzophenone at 0.1−2.0 wt % are generally lower than the corresponding log K_{ow} values.[25] This could be explained that *n*-octanol engages in van der Waals, polar, and (weak) hydrogen-bonding interactions because of its aliphatic structure, whereas PE can only undergo van der Waals interactions with the UV stabilizers.[44] Furthermore, PE is a semicrystalline polymer with amorphous and glassy regions;[45] thus, the polymer does not have the "liquid-like form" of *n*-octanol. The log K_{LDPEw} values were generally >5 for the selected UV stabilizers, indicating that their release from the LDPE fibers was very slow. We previously reported slight deviations (i.e., a difference within 1 log unit, except for UV329) between the K_{LDPEw} values computed using the subcooled liquid solubility and partitioning between LDPE and the cosolvent mixture (ACN/water, 4:6 v/v).[22] The experimental data (Table S5) support the usefulness of the cosolvent method for estimating the water-solubility of highly hydrophobic chemicals.

Internal Diffusion Coefficients of UV Stabilizers within LDPE Phase. Figure S8 (SI) shows the concentrations of the target UV stabilizers that were used to estimate the internal diffusion coefficients (D_{LDPE}, m^2 s^{-1}) of the UV stabilizers in the LDPE sheets by fitting the data to eq S3 (SI). The log D_{LDPE} values (m^2 s^{-1}) obtained for the five selected UV stabilizers in LDPE ranged from −13.5 to −14.4 (Table S5, SI), indicating that the target UV stabilizers diffused slowly in the LDPE matrix. To the best of our knowledge, this is the first study to measure the diffusion coefficients of these five UV stabilizers in LDPE. For risk assessment of MP-associated additives in aquatic environments, the internal diffusion coefficients can also be obtained from mathematical models, assuming that the leaching of plastic additives into the surroundings is controlled by internal diffusion.[16,17,40] However, the internal diffusion coefficients may vary depend-

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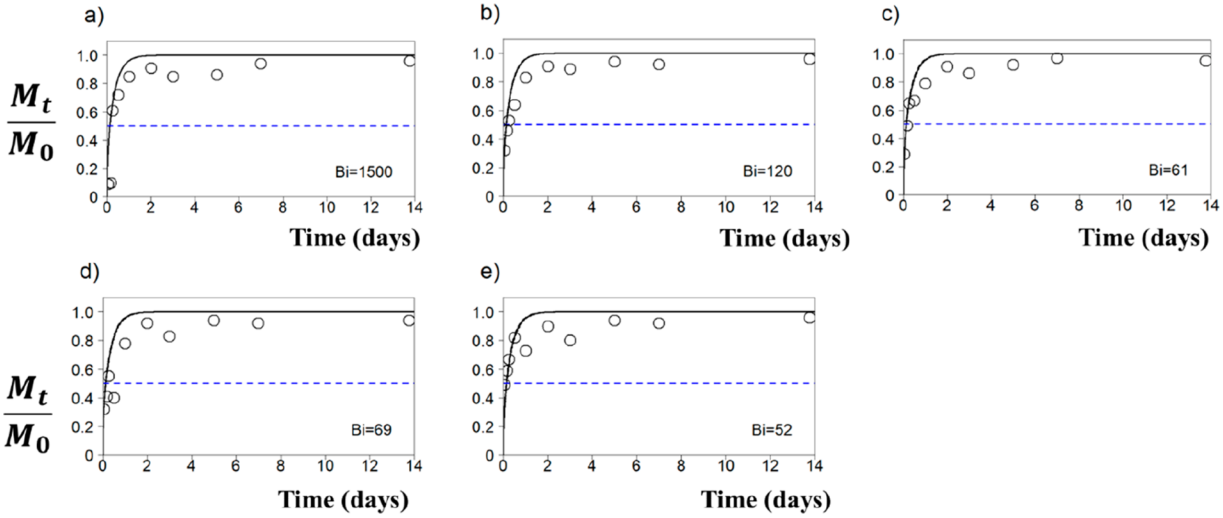

Figure 3. Fraction of UV531 leached from LDPE fibers into ACN/water (4:6, v/v) mixture at desorption time (t) for ω = (a) 0.1, (b) 0.2, (c) 0.5, (d) 1.0, and (e) 2.0 wt %. Comparison of the experimental concentration of UV531 (empty circles) in plastic fibers. Line values were predicted using eq S4 where δ_w = 10 μm (dashed lines), 50 μm (solid lines), and 100 μm (dotted lines). Biot numbers were calculated at δ_w = 50 μm; blue dashed line indicates the half-leaching amount of the UV stabilizers.

ing on the estimation methods.[40] Precise determination is more important for moderately hydrophobic chemicals (log K_{ow} 3−4), for which diffusion is mainly controlled by internal diffusion, whereas diffusion at the ABL is the rate-limiting factor for more hydrophobic chemicals.[14]

Kinetics Model of the Leaching of Five Selected UV Stabilizers from LDPE Fibers. The leaching of additives from plastics to the surroundings depends on several factors, including the nature of the polymer, additives, the relationship between the polymers and additives, and the nature of the surrounding medium.[46] Herein, the extent and lifetime of the release of the plastic additives were interpreted using the one-dimension convection−diffusion model by applying the D_{LDPE}, K_{pw}, and rate of mass transfer through the ABL, which are fundamental physicochemical parameters.[15] In this model, the thickness of the ABL, δ_w, was assumed to be in the range of 10−100 μm, corresponding to high and low levels of environmental turbulence. The δ_w under gentle agitation with a stirring bar was estimated to be between 50 and 100 μm.[15,47] The δ_w values were used to calculate the mass transfer Biot number (Bi), which is a key parameter in the leaching model (eq S6), defined as the ratio of the mass transfer rate via diffusion to the mass transfer rate in a fluid medium.[15,43]

Figures 2, 3, and S9−11 (SI) show the experimental kinetic data for leaching of the target UV stabilizers from the LDPE fibers into ACN/water (4:6, v/v) at a mass fraction from 0.1 to 2.0 wt %. The experimental and predicted data agree well at estimated δ_w (i.e., 10, 50, and 100 μm) and mass fraction values of 0.1−0.5 wt % for UV 326, UV327, UV328, and UV329 and 0.1−2.0 wt % for UV531 (Figures 2a−c, 3a−e, S9a−c, S10a−c, and S11a−c). However, the theoretical predictions cannot explain the experimental leaching kinetics data for the four benzotriazoles at mass fractions of 1.0 and 2.0 wt % (Figures 2d,e, S9d−e, S10d−e, and S11d−e). These agree with good linear relationships between mass fraction and the leaching concentration in ACN/water (4:6, v/v) only at 0.1−0.5 wt % for the four selected benzotriazoles and at 0.1−2.0 wt % for benzophenone in our previously reported.[22] Notably, the SEM images showed a precipitate layer on the LDPE fibers containing 1.0 and 2.0 wt % of UV 326, UV327, UV328, and UV329, as mentioned in the previous section (Figure 1e,f, S1e,f, S2e,f, and S3e,f). The degree of crystallinity of the LDPE fibers also increased as the concentration of UV326 in the LDPE fibers increased (Table S4 and Figure S6; see the SI). This highlights two regimes: leaching of UV stabilizers from the LDPE fibers when the solubility in the polymer phase is (1) below the saturated concentration and (2) higher than the saturated concentration, forming a crystal layer of UV stabilizers on the LDPE fiber surface ("blooming" phenomenon).[12]

In Case I (Figures 2a−c, S9a−c, S10a−c, and S11a−c), when ω = 0.1−0.5 wt % for the four benzotriazoles and over the entire investigated ω range for benzophenone (see Figure 3a−e), the LDPE fibers contained a single UV stabilizer as a homogeneous solution. Thus, the solubility of the UV stabilizers in the LDPE polymer is lower than the saturated concentration. The leaching of UV stabilizers from LDPE fibers includes two distinct processes: (1) diffusion toward the polymer surface and (2) subsequent transfer through the ABL. This causes the concentration of the UV stabilizer on the fiber surface to be maintained at zero or causes the layer of precipitate on the fiber surface to dissolve rapidly, which follows Fickian diffusion. Considering leaching under finite boundary conditions, eq S4 (SI) is applicable, where D_{LDPE} is considered a constant.

In Case II (Figures 2d,e, S9d,e, S10d,e, and S11d,e), UV326, UV327, UV328, and UV329 emerged on the surface and formed a new phase. As discussed in our previous study,[22] the solubility of a solid additive in a polymer solution is determined by the free energy of mixing (ΔG_{mix}) of the additive at its subcooled liquid state and the polymer segments. When the melting point of a plastic additive is below that of the polymer and the concentration of the additive in the polymer exceeds its solubility, the additive precipitates either in the polymer matrix or on the polymer surface ("blooming"). Because no cases of internal precipitation were reported,[12] the "dissolved" concentration of the additive in LDPE should be equal to the saturation solubility of the additive. Assuming that the "dissolved" concentration of the additives is uniform throughout the polymer solution at equilibrium, the concen-

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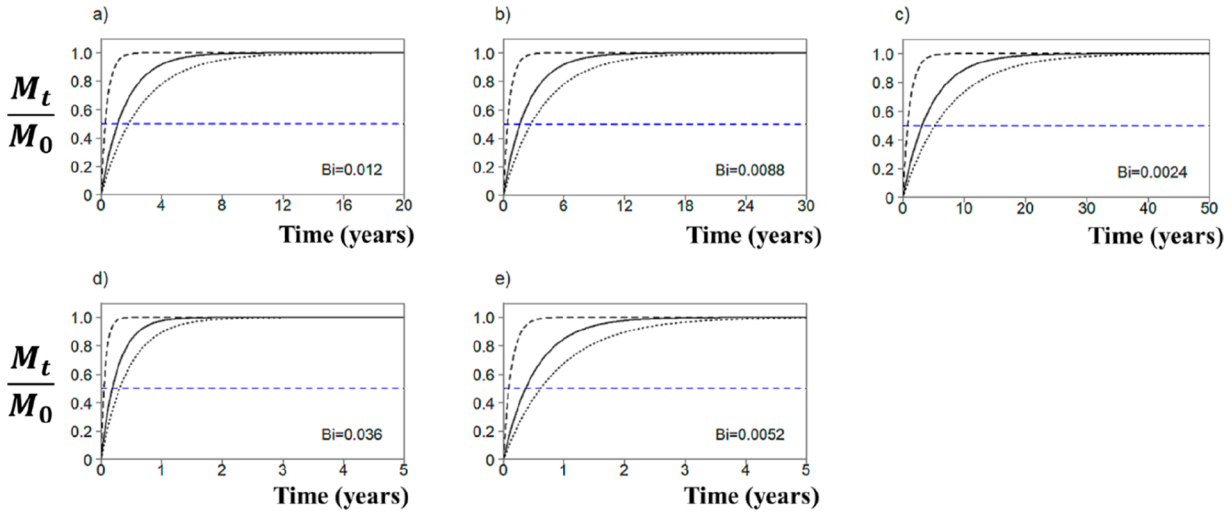

Figure 4. Fraction of (a) UV326, (b) UV327, (c) UV328, (d) UV329, and (e) UV531 (mass fraction ω = 0.5%) leached from LDPE fibers into water at time t. Line values were predicted using eq S4 where the thickness of the aqueous boundary layer (δ_w) is 10 μm (dashed lines), 50 μm (solid lines), and 100 μm (dotted lines). Biot numbers were calculated at δ_w = 50 μm; the blue dashed line indicates the half-leaching amount of the UV stabilizers.

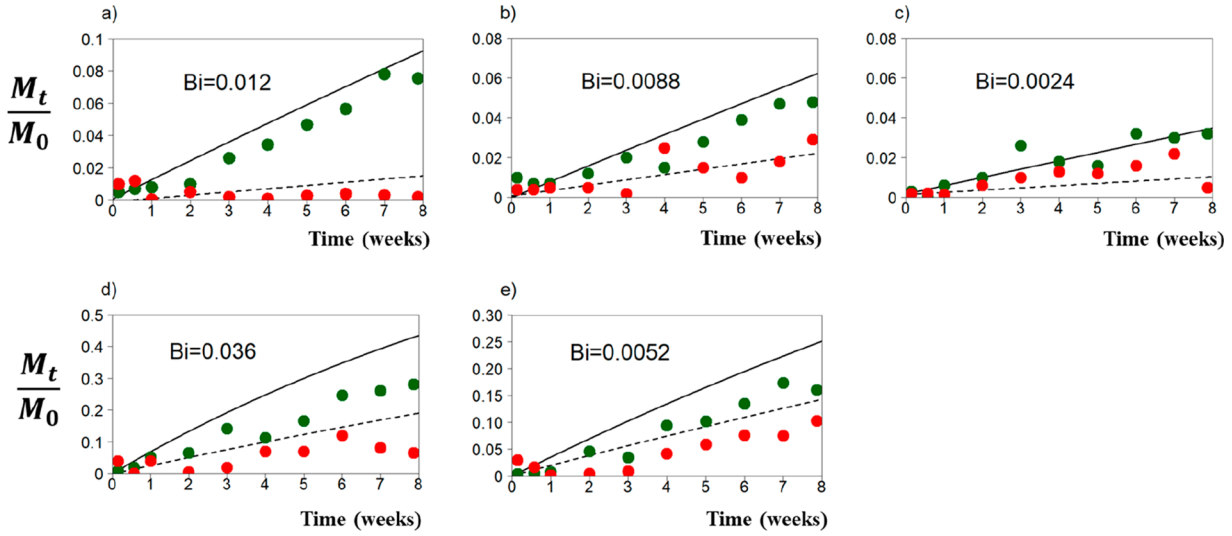

Figure 5. Fraction of (a) UV326, (b) UV327, (c) UV328, (d) UV329, and (e) UV531 leached from LDPE fibers into water at time t. Line values were predicted using eq S4 for the LDPE fibers containing the UV stabilizers at 0.5 wt % (solid line) and 2.0 wt % (dashed line) where the thickness of the aqueous boundary layer (δ_w) is 100 μm. Biot numbers were calculated at δ_w = 50 μm. The experimental data for leaching of the five target UV stabilizers into water are indicated by green dots at 0.5 wt % and red dots at 2.0 wt %.

tration of the additives at the polymer surface should be lower than the saturation solubility if the precipitated crystalline layer is removed from the surface. Then, the leaching mechanism can be equivalent to that of Case I.[12] If the additive dissolves well in the adjacent medium, the crystal layer on the polymer surface can be removed quickly with a very high mass transfer rate, internal diffusivity could be the only required parameter, and the mathematical model based on intraparticle diffusion is applicable,[14] exemplified by the desorption of organic chemicals into a high content of organic matter or gut fluid medium.[17,18,48] For hydrophobic organic plastic additives, such as UV stabilizers, leaching into water, therefore, not only depends on diffusion in the plastic phase or across the aqueous boundary layer but is also limited by the formation of a precipitation layer on the polymer surface. Therefore, it may be difficult to determine the leaching half-life.

Based on the observations, the one-dimensional convection−diffusion model was also applied to evaluate the kinetics of leaching of the five target UV stabilizers into water at 25 °C at a mass fraction of 0.5 wt %. Using the experimentally determined K_{LDPEw} and D_{LDPE}, the leaching kinetics of the five selected UV stabilizers were predicted using eq S4 (Figure 4). With very low D_{LDPE} and high log K_{LDPEw} values, leaching of the five target UV stabilizers was expected to occur over a long time. The obtained leaching lifetimes were approximately 30, 20, 12, 3, and 2 years for UV328, UV327, UV326, UV531, and UV329, respectively, at δ_w = 50 μm. The calculated Bi were 0.0024−0.036 based on eq S6, indicating that diffusion through the ABL was the rate-limiting step for the five hydrophobic UV stabilizers. This is consistent with prior observations of the desorption of polychlorinated biphenyls (PCBs) from PE pellets[14] and pentachlorobenzene from PE and PP films.[15] The leaching half-life was observed at varying

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δ_w values under well-stirred and unstirred conditions. At δ_w = 10 μm, half of UV329 leached into the water within a few weeks, whereas UV531, UV326, UV327, and UV328 required 1, ~2, 4, and 8 months, respectively. The leaching half-lives of UV326, UV327, UV328, UV329, and UV531 became longer (~1, 1.5, and 3 years and 1.5 and 4 months, respectively) at δ_w = 50 μm, compared with 1.8, 3, and 5 years and 2 and 7 months, respectively, at δ_w = 100 μm (Figure 4). To validate the predicted model, experimental data for leaching of the five UV stabilizers into water at mass factions of 0.5 wt % (Case I) and 2.0 wt % (Case II) are plotted in Figure 5, considering the short experimental time (8 weeks) and low concentration of the target UV stabilizers leached from the LDPE fibers into water. The experimental data are consistent with the prediction model having *Bi* values <1, indicating that diffusion in the ABL is the rate-limiting step. Furthermore, the differences between the experimental leaching kinetics at mass fractions of 0.5 and 2.0 wt % were not significant. However, leaching at 0.5 wt % was generally higher than that at 2.0 wt %, supporting the deduction that leaching of the plastic additives in Case II might be slower than that in Case I owing to the precipitate layer formed on the surface of the LDPE fibers at 2.0 wt %.

The *Bi* values (>1) for leaching of the additives into ACN/water (4:6, v/v) were much higher than those for leaching into water, possibly because of the higher solubility of the target UV stabilizers in the cosolvent mixture than in water, indicating that leaching of the target UV stabilizers into the cosolvent mixture was dominated by diffusion within the LDPE fibers. This supports the hypothesis that during interactions between plastics and aquatic environments hydrophobic organic plastic additives (contaminants) are enriched in media high in organic matter,[48] such as the stomach oil of seabirds, fish oil,[17,18,49,50] or the digestive tract,[10] where diffusion in the plastic phase is likely the rate-determining step. Therefore, the leaching kinetics of a hydrophobic plastic additive depend on its solubility both in the polymer phase and in the surrounding medium. Note that leaching of the five selected UV stabilizers from the LDPE fibers was characterized by high log K_{LDPEw} and low D_{LDPE} values. Thus, leaching could occur even slower than the degradation of LDPE,[43] which suggests that these chemicals are likely to be transported along with LDPE MPs instead of leaching out into water.[20]

Implications for the Environmental Fate of Hydrophobic UV Stabilizers. This study provides a fundamental understanding of the kinetics of leaching of five UV stabilizers (at different mass fractions) from LDPE (micro)fibers into water, as well as reference values (i.e., D_{LDPE} and K_{LDPEw}) and leaching time scales. At low mass fractions (i.e., ω < 0.5 wt %), although the studied UV stabilizers have extremely low D_{LDPE} and very high K_{LDPEw} values, indicating limited transport in water, the leaching half-life of the UV stabilizers from microscale plastic debris might be a few months to years, depending on the chemical properties, size of the MPs, and turbulence of the water. With a long leaching half-life in water and high hydrophobicity, UV stabilizers should be considered as persistent and potentially bioaccumulative chemicals in aquatic environments. Moreover, owing to their hydrophobicity and extremely low solubility, UV stabilizers are expected to adsorb to other environmental compartments (i.e., suspended particulate matters and sediment), limiting their transport as "dissolved phase" in water.[22] However, the leaching and environmental transport of the UV stabilizers from/via plastic debris might occur in parallel, which could partly explain the detection of these substances in some remote regions.[50,51] Notably, leaching of the five target UV stabilizers into water at higher mass fractions (i.e., ω = 2.0 wt %) was not scrutinized in this study because this process also depends on the removal rate of the crystal layer on the surface of the LDPE MFs, which is expected to be longer than that of homogeneous LDPE MFs (i.e., ω = 0.5 wt %).

Leaching of the five hydrophobic UV stabilizers into water depends on their diffusion through the ABL (*Bi* values $\ll$1). However, in a strongly dissolving medium with *Bi* values >1 (e.g., fish oil, digestive tract[17,18]), diffusion within the plastic may be the rate-determining step. The rate-determining step should be considered when using the model to estimate the leaching half-life, physicochemical properties (i.e., partition and diffusion coefficients), and mass loss of plastic additives in aquatic environments, particularly in the case of MPs with a crystal layer of hydrophobic additives covering the surface when the layer is removed very quickly in a rich organic matter medium. To assess the bioavailability or risks in aquatic environments, it is essential to consider the mass fractions of plastic additives and their leaching kinetics.[15] Quantitative data on the intrinsic properties of the additives and polymers, solubility of the additives in the polymer solution, and solubility of the additives in the contacting medium are required to gain a better understanding of the leaching kinetics of plastic additives in aquatic environments.

Notably, the leaching kinetics of the five selected UV stabilizers at 25 °C is considered the simplest case without any effects from external factors (i.e., weathering processes, pH, dissolved organic matter, salinity, and temperature), which is not reflective of real-world conditions, in which MPs are affected by external stresses (i.e., sunlight,[52] mechanical forces,[53] temperature,[54] and microorganism attack[55]), which could lead to surface modification of the MPs and interaction between the additives and polymers, consequently altering the leaching kinetics of the plastic additives.[43,56−58] Moreover, because the half-life for plastic degradation is expected to be approximately 100 years,[54,59] leaching half-lives longer than 100 years might have limited meaning under real environmental conditions. Therefore, actual leaching is expected to be dominated by environmental factors rather than diffusion processes, with diffusion as the limiting factor. Future studies should consider the effects of dynamic weathering conditions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.3c06817.

Additional information on chemicals and materials used, experimental details and methods for X-ray diffraction, partition coefficients K_{LDPEsm} and K_{PDMSsm}, film-stacking experiments, desorption kinetics, kinetics model, instrument analysis, and detailed experimental data (PDF)

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Notes

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■ ABBREVIATIONS

UV, ultraviolet; LDPE, low-density polyethylene; K_{LDPEw}, partitioning between LDPE fibers and water; D_{LDPE}, internal diffusion coefficient; K_{ow}, *n*-octanol/water partition constant; MPs, microplastics; MFs, microfibers; HDPE, high-density polyethylene; PP, polypropylene; PVC, polyvinyl chloride; HOCs, hydrophobic organic chemicals; ABL, aqueous boundary layer; PCBs, polychlorinated biphenyl; HCHs, hexachlorocyclohexane; CBs, chlorinated benzenes; BFRs, brominated flame retardants; UV326, 2-(5-chloro-2*H*-benzotriazol-2-yl)-4-methyl-6-(2-methyl-2-propanyl)phenol; UV327, 2,4-di-*tert*-butyl-6-(5-chloro-2*H*-benzotriazol-2-yl)phenol; UV328, 2-(2*H*-benzotriazol-2-yl)-4,6-bis(2-methyl-2-butanyl)-phenol; UV329, 2-(2*H*-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol; UV531, (2-hydroxy-4-octoxyphenyl)phenylmethanone; OECD, Organization for Economic Co-operation and Development; ACN, acetonitrile; PDMS, medical-grade polydimethylsiloxane; SEM, scanning electron microscopy; EDS, energy dispersive X-ray spectroscopy; XRD, X-ray diffraction; LC-MS/MS, liquid chromatography with tandem mass spectrometry; FTIR, Fourier-transform infrared (FTIR) spectroscopy; ω, mass fraction

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