

Implications of a New Test Facility for Fragmentation Investigations on Virgin (Micro)plastics

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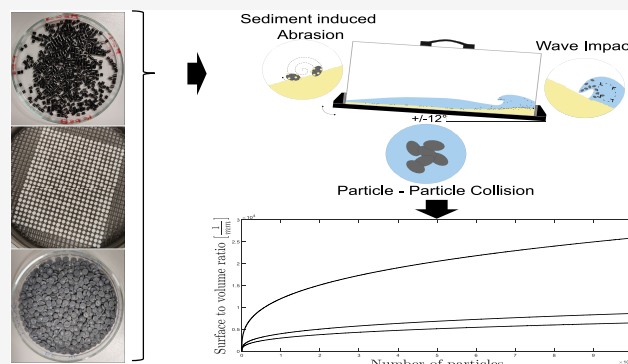
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ABSTRACT: Littered plastics are partly introduced into water bodies, ultimately transporting this waste to the shores and oceans. At the shore, ultraviolet (UV) radiation (also present in other environmental compartments) and wave breaking cause plastics to degrade and fragment into smaller particles, called microplastics, if below 5 mm. Since these plastics' surfaces can act as vectors for hydrophobic (toxic) chemical substances (e.g., per- and polyfluoroalkyl substances (PFAS)) and leach (toxic) chemicals into the water, the increase in the surface area through the fragmentation of plastics becomes relevant. Studies investigating different effects on the fragmentation of plastics have mostly disregarded a sufficient mechanical component for fragmentation, focusing on degradation by UV radiation. Therefore, this study investigated the impact of the mechanical fragmentation drivers, wave impact, and sediment abrasion on the fragmentation of expanded polystyrene (EPS), high-density polyethylene (PE-HD), and polyethylene terephthalate (PET) particles. In a newly designed test facility called Slosh-Box, the mentioned impacts were investigated concurrently. The results reveal that the mechanical impacts alone are sufficient for plastic fragmentation, and the test facility is suitable for fragmentation investigations. Furthermore, the increase in surface area was determined via scanning electron microscopy. For EPS, the surface area increased more than 2370-fold, while for PE-HD and PET, surface areas increased between 1 and 8.6 times. Concluding from the results, the new test facility is suitable for plastic fragmentation studies. In addition, sediment was revealed to be a relevant fragmentation driver, which should be included in every experiment investigating the fragmentation of plastic in a nearshore environment independent of other drivers like UV radiation.

KEYWORDS: microplastic, microplastic fragmentation, physical model experiments, new test facility, mechanical impacts on microplastic, active surface of microplastic particles



1. INTRODUCTION

Through media, microplastics (MP) are gaining an increasingly prominent and present role in society, especially as a general indicator of anthropogenic environmental influence. However, the impact of these plastic particles, which are between 5 mm and 100 nm in size, on ecosystems and organisms has not been sufficiently investigated.^{1–4} Many studies examining the adverse effects of exclusively microplastics (disregarding co-contaminants) on organisms are working with increased concentrations compared to the environment. Contrary to this, several investigations could not find a negative impact of virgin microplastics on organisms, although increased concentrations were used, making a threshold value hard to define.^{4–8} Thus, although microplastics have been detected in numerous biota captured directly from the environment, little proof supports that the environmental concentrations of microplastics cause adverse effects on these organisms.⁹ However, persistent organic pollutants (POPs), mostly disregarded in MP toxicity studies, can adhere to the surfaces of (micro)-

plastics due to their hydrophobic properties.^{10–12} Organisms can ingest these POPs through MP consumption, causing adverse effects.^{8,10,13} In addition, a trophic accumulation of microplastics or pollutants partially adhering to them has been observed but has not yet been sufficiently investigated. Generally, studies on this topic have contradictory statements, proving and refuting the trophic accumulation of microplastics in organisms, while the effect is proven for several POPs, e.g., PFAS and other toxic sorbates.^{14,15}

The uptake by organisms also occurs more frequently with increasing concentrations of microplastics in water. This increase is mainly caused by constantly rising production

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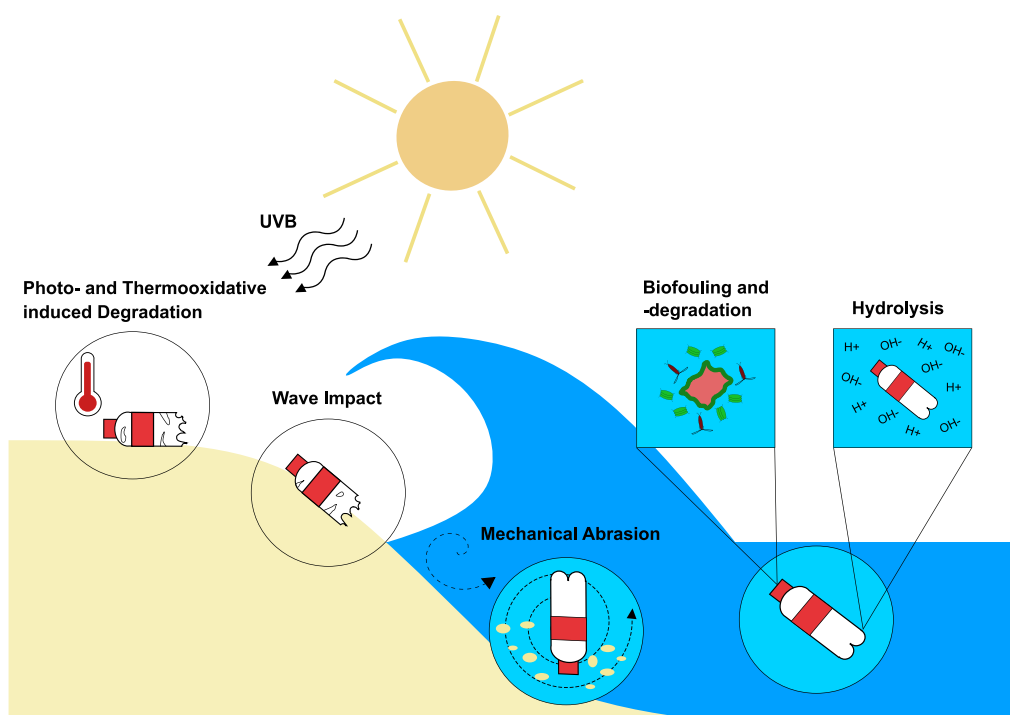


Figure 1. Degrading and fragmenting influences in a beach environment.

volumes of plastics, which result in a proportionally higher waste input into water bodies and, thus, oceans.^{16–18} No significant change in concentrations of microplastics in oceans was measured throughout the years, supporting the idea of microplastics eventually depositing in deep-sea sediment.¹⁹ On the other hand, a study by Pabortsava and Lampitt (2020)²⁰ found that previous studies severely underestimated the microplastic concentration in the oceans.^{19–21} With a constant input of plastics into water bodies, the total concentration of (micro)plastics in the oceans increases since it takes several decades to centuries for their complete mineralization (input quantity > mineralized quantity).^{22,23} Based on this trend, it can be assumed that microplastic concentrations that are harmful to organisms might be reached.²⁴

Although the ocean floor, gyres, and specific zones in between are considered final sinks for littered plastics, most are initially trapped near the coast or shore by onshore winds, waves, and currents immediately after exiting streams and rivers.^{25–31} Via the different degradation pathways, UV-irradiation, thermo-oxidation, biological degradation, and hydrolysis, the littered plastic waste is continuously fragmented by mechanical forces (Figure 1).^{23,32–34} Since there are different definitions for “degradation”, it is defined here as an alteration of the polymer’s chemical structures and physical properties. Other sources include the mechanical breakdown of plastics without changes in the polymers’ structures and properties in the degradation definition.³⁵

This constantly progressing comminution of the polymers exponentially increases the total surface area of the plastics present in the oceans (Figure 2). Thus, with declining size, plastic can bind relatively more pollutants to its surface, which organisms could ingest, causing damaging effects and possibly accumulating in their organs.³⁶ Furthermore, the increase in surface area also leads to increased leaching of additives from the plastics, which, in addition to the pollutants and direct influences, plays a central role in the potential environmental

damage caused by microplastics.^{37–39} It is, therefore, useful to determine a rate for the increase in plastics’ surfaces through degradation and mechanical wear, ergo the fragmentation over time.

Since biodegradation and hydrolysis are comparably slow processes and thermo-oxidation is negligible in a nearshore environment due to the water’s cooling effect, most studies dealing with fragmentation or degradation focus on abiotic decomposition by photo-oxidation and direct photolysis. However, a mechanical influence is always necessary to form microplastics.^{40–54} This partial focus results from the complex task of modeling a natural environment while the aforementioned processes, mechanical abrasion and UV-irradiation, remain independently adjustable. Especially the simulation of a shore environment poses a difficult task since, among other influences, wave breaking, sediment, UV radiation, and saltwater have to be considered in a closed abstract model simultaneously.³⁴ Nevertheless, it would be helpful to simulate the multitude of degrading and fragmenting impacts a beach combines in parallel since it is often considered a hotspot for microplastic formation.^{32,55}

Trying to simulate a beach environment, Song et al. (2017)⁴⁴ examined mechanical force and UV successively but deliberately disregarded a possible relevant synergy effect with simultaneous exposure. After UV irradiation, the plastic parts and beach sand were mixed and rotated in glass bottles for 2 months. However, no water was used. The results showed UV-weathered plastic fragments to a greater extent and faster than non-weathered plastic. Song et al. (2017)⁴⁴ also stated that mechanical abrasion (MA) is generally difficult to approximate and that their results can only be applied to a beach environment to a limited extent. They point out that more research is needed on factors such as wave breaking and saltwater influence. Furthermore, they found that the fragmentation of plastics is favored by degradation, i.e., the internal decomposition of the material, but that it is not a

Table 1. Polymers Used in the Tests^c

plastic type	density [g/cm ³]	shape	dimensions [mm]	SA [mm ²]	NIS ^a [kJ/m ²]	color	producer
EPS	0.023	spherules	$d = 4-5$	ca. 64	$\ll 1$ N.A. ^b	white	Rayher Hobby GmbH
PE-HD	0.936	lentils	$d = 5$ $h = 1.3$	ca. 60	ca. 20 ^b	gray	MULTIPET Kunststoffe
PET	1.43	cylinders	$d = 2.5$ $h = 3$	ca. 38	ca. 3 ^b	black	Innovative Kunststoffveredelungs- GmbH

^aNIS stands for notch impact strength. ^bLiterature value (no information granted by the producer). ^cDensities were determined according to ref 66. EPS density as stated by the producer. SA was calculated according to the shape.

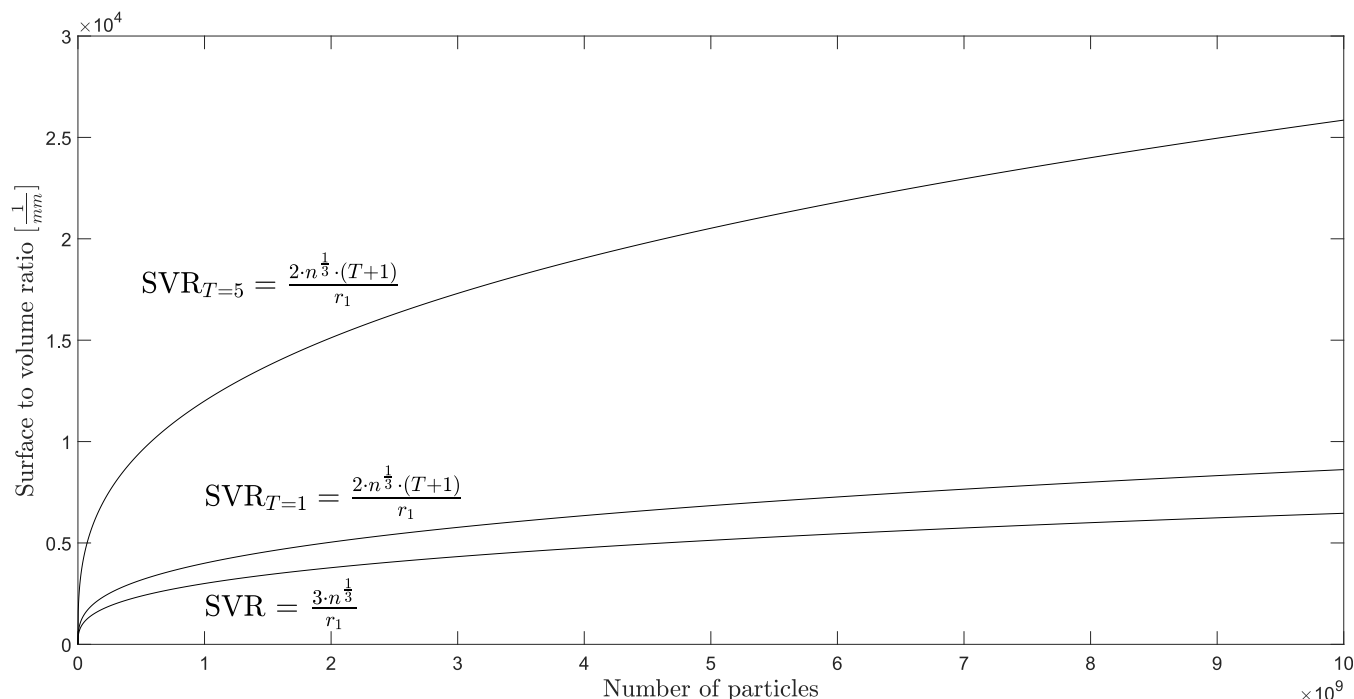


Figure 2. Surface-to-volume ratio (SVR) increase through the theoretical partition of a sphere or cylinder/flake with a radius $r_1 = 1$ mm into n spheres with a radius r_n and cylinders into n cylinders/flakes with a thickness $(1/T)$ of $1/1$ and $1/5$ of the radius r_n .

premise for the process. Since UV irradiation lies beyond the scope of this paper, it will not be further evaluated here.

The primary degradation and fragmentation driver, UVB-irradiation, is reduced during winter (for northern hemisphere countries). Thus, recently littered plastic is barely degrading, resulting in a prevalence of MA as the main fragmentation driver in the marine environment.⁵⁶ Efimova et al. (2018)⁵⁷ and Chubarenko et al. (2019)⁵⁸ demonstrated by physically modeling nearshore wave patterns that even product-new plastic partially fragments after a short time. In the experiments, low-density polyethylene (PE-LD), polystyrene (PS), polypropylene (PP), and EPS were investigated by rotating the polymers, sediment of different grain sizes, and water in a modified concrete mixer. Within 24 h, fragments of each type of plastic could be found. In addition, the tests revealed the dependence of the fragmentation rate on the sediment grain size. The fragmentation rate describes the mass percentage of fragments generated over a specific timespan to the initial mass of the polymers used.

However, only a short and intense sediment movement was considered in their tests. Minor MA caused by non-storm waves is often described as a negligible influence for plastic fragmentation without former UV degradation.⁴⁴ To our knowledge, no studies have been carried out in parallel in long-term tests that have investigated particle–particle–collision,

particle–sediment–collision, and wave-breaking influences on the fragmentation of microplastics. Since these conditions are predominant at beaches, microplastic research has to close this knowledge gap by evaluating if minor MA alone leads to a measurable fragmentation of virgin plastics in a nearshore environment and, if so, quantify the influence. However, the thus-determined fragmentation is not directly applicable to weathered plastics.⁵⁹

To properly answer the research question, a new test stand had to be developed, and three environmentally representative plastic types (high-density polyethylene (PE-HD), polyethylene terephthalate (PET), and expanded polystyrene (EPS)) were investigated. These plastics served as indicators of whether the new test stand was suitable for the investigation and, if so, as samples to quantify the influence of the test stand on their fragmentation. Although EPS has a relatively low mass fraction of the plastic waste found on beaches, it represents a considerable proportion of the number of particles found.⁶⁰ This discrepancy is because of the low density of EPS and the possibility of the particles disintegrating faster due to a lower intrinsic strength than other plastics.⁴⁴ In contrast to EPS, PE is the plastic most commonly found on beaches by mass. About 23 percent of the plastic waste in the aquatic environment consists of PE.⁶¹ However, local factors like industrial activity or ports can cause a deviation from the

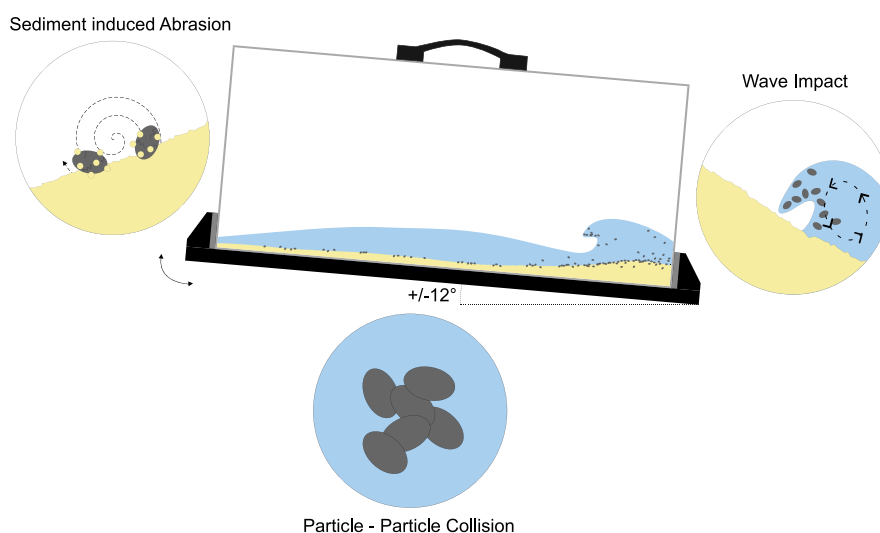


Figure 3. Mechanical fragmentation drivers the slosh box simulates.

average.^{60,62} Due to the direct contact with the sediment layer, the dominant mechanical forces substantially impact PET. Furthermore, according to Chubarenko and Stepanova (2017),⁶³ plastics with higher densities than salt water can enter the sediment layer and thus are protected against both influences, mechanical abrasion, and wave breaking. Therefore, a beach environment was simulated over 90 days each for the different plastic types in the newly developed test stand. The simulation investigated only the mechanical force impact on plastic by wave breaking, sediment–particle–collision, and particle–particle–collision. The experiments also included a variation in sediment grain sizes. The objective of the investigation was first to develop a new test stand for microplastic fragmentation, which includes several MA drivers, and assess its suitability. The second scope was using the test stand to determine the samples' surface area increase and their fragmentation rate in dependence on the prevailing mechanical influences.

2. MATERIALS & METHODS

The experiments investigated and quantitatively evaluated the relevance of wave breaking, sediment-, and particle-induced abrasion for fragmentation of plastics in the near shore environment and the hereby evoked increase in surface area in proportion to their initial surface area (Table 1, Figures 1–4). As a function of wave characteristics like speed, height, and turbidity, waves can lift polymer particles and break down on and with them at the shore, depending on the plastic's density.^{57,64} This process is the driving force for all subsequent

mechanical abrasions. Furthermore, besides the impact of the breaking wave, waves transport sediment particles or resuspend them when breaking onto the beach, causing a collision of plastic and sediment particles, leading to the abrasion of the plastic. In addition, plastic particles collide with each other, possibly resulting in abrasion as well. These processes cause continuous fragmentation and the generation of microplastics.⁵⁸

The influences of wave breaking and sediment abrasion were therefore tested individually and in combination to evaluate possible synergy effects more precisely. In addition, in contrast to most studies, salt water was used as the surrounding medium.^{48,58,65}

2.1. Apparatus. The investigations were carried out in a modified Slosh-Box (Figures 3 and 4), serving as a new test stand. It consists of a static support structure of square aluminum profiles (Figure 4a) and a swivel table (Figure 4b). The swivel table is driven alternately up to a maximum inclination of $\pm 12^\circ$ by a 250 W electric motor, which can be regulated via a control panel (Figure 4c). Three boxes with a volume of 20.25 L each ($L = 450$ mm; $W = 300$ mm; $H = 200$ mm) are mounted on the swivel table and can be closed by a lid (Figure 4d). For the permanent operation of the Slosh-Box, the total mass of the boxes must not exceed 40 kg. The maximum load of the apparatus, with full loading and maximum deflection, is 26 complete movements (i.e., an angular work of 48° per movement) per minute. The boxes used for the investigations were constructed with polymethyl methacrylate (PMMA). The advantages of PMMA boxes are the possibility of observing the tests and the stability and resistance against external influences. The often-described problem of contamination when using plastics as a test stand could be excluded via different colors and densities of the sample material and PMMA.

The Slosh-Box was placed in a light-proof and leveled climate chamber, which maintained the temperature at 22°C during the experiments, blocked UV radiation, and kept the water level in the boxes consistent.

2.2. Plastics. Polymers strongly differing from each other in density were chosen to compare the behavior of highly buoyant (EPS), buoyant (PE-HD), and sinking (PET) particles in saltwater in the Slosh-Box (Figure 5). The

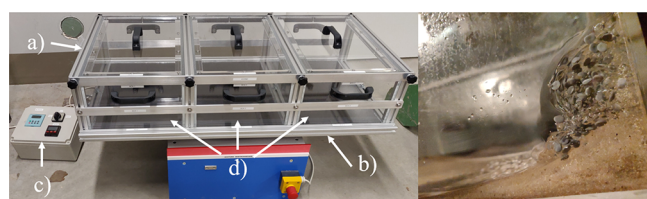


Figure 4. Slosh-Box apparatus (left) ((a) static support structure; (b) swivel table; (c) control panel; (d) boxes with lids) and side view (right) during operation with PE-HD pellets and 0.25–0.5 mm sand grains.

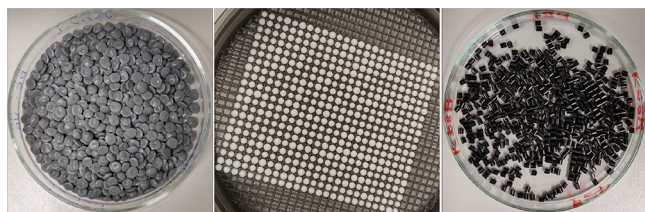


Figure 5. PE-HD- (left), EPS- (middle), and PET-particles (right) used for the experiments.

deviations in density caused different interaction intensities with the sand and waves since the duration and depth of submersion in the saltwater varied. The properties of the plastics used for the tests are listed in Table 1. In addition, the uniformity of shapes across all plastic types was subordinate to the plastics with the highest uniformity in a plastic class, thus increasing the results' robustness. Section 3 is further elaborating on this issue.

2.3. Test Settings. For the experimental setup, 1.5 L of salt water (1538 g; salinity 35‰) and approximately 2.2 kg of sand (1 cm layer thickness in the boxes) in different grain sizes (0.25–0.5 mm; 0.5–1 mm; 1–2 mm) were used per test box. The alternating movement of the Slosh-Box caused the sediment to distribute to the boxes' sides quickly. Nevertheless, a sediment layer covering the bottom remained throughout the experiments. For each box, the plastic pellets were added in a quantity that ensured a statistically secured interpretation of the evaluation; for PE-HD, 525 pellets (≈ 16 g), for PET, 525 particles (≈ 11.5 g), and for EPS, 525 spherules (≈ 0.575 g) per box. Before the tests, all virgin plastic particles were gently cleaned in an ethanol/deionized water solution using a magnetic stirrer on a low rpm setting (no particle touched the magnet) to avoid mass deviations through production residues on the pellets. Subsequently, the particles were dried in an oven at 40 °C until mass constancy ($\Delta m < 0.1$ mg) was reached, weighed, and added to the test setup.

The tests were carried out for 90 days for each sediment size and plastic, and an intermediate result was evaluated every 30 days. During 90 days, about 6.7 million beach run-ups and wave breakings were simulated. The test period of 3 months was chosen to avoid the influence of biofouling, the process of tiny algae and organisms adhering to the plastic that would occur in nature after this period at the latest.^{67–69}

2.4. Boundary Conditions. In order to consider wave breaking and abrasion separately, the influences of the boxes' wall and saltwater were evaluated in different test series. Saltwater poses a problem regarding mass due to the adhesion of crystalline salt on the plastic particles. Therefore, samples were placed in salt water without wave movement or sediment to evaluate this effect separately and otherwise evaluated identically. In the test evaluation, the adhering salt was carefully and gently removed by a washing process (see procedure test evaluation), and no mass gain was measured.

The boxes' walls also represented a deviation from a natural beach environment due to the slight impact of the plastic particles on them during the tests. However, isolating and measuring this effect was impossible since several factors like wave breaking and particle–particle collision could not be excluded in any possible setting. Nonetheless, this effect only posed a minor impact since wave breaking and sediment abrasion dominated the fragmentation of the particles, as pre-tests with and without sediment ensured. The pre-tests were

conducted for 1 month and with similar settings to the main experiments (which were derived from the pre-tests). Furthermore, water favors the hydrolysis of plastic. However, this influence is negligible compared to the dominant forces, especially in the given timeframe.^{50,51}

2.5. Evaluation. After each period (30 days), all plastic particles were isolated (gently wet-sieved or manually) and carefully cleaned in a mixture of ethanol and deionized water via a magnetic stirrer on low rpm settings (sufficient to move the particles in the solution, without them touching the magnet). The plastic particles were dried at 40 °C until their mass remained constant (± 0.1 mg). The effectiveness of the cleaning and drying process was validated in pre-tests, as no mass increase was measurable with virgin material (< 0.1 mg) after 30 days in salt water, concluding that no salt adhered to the plastics.

The experiments were first mass-evaluated to determine the microplastic fragmentation rate. The underlying assumption was that the difference in mass before and after the tests equals the mass of generated microplastics. However, while sieving, it was observed that the resulting fragments were smaller than the smallest sieve mesh size (0.063 mm). Therefore, scanning electron microscopy (SEM) was used to estimate the fragments' sizes, their surface area (from 0.1 to 500 μm fragment diameter) and assess the surface damage on the parent particles. An SEM Flex SEM 1000 by HITACHI was used for imaging with an accelerating voltage of 5 kV, working distances between 4500 and 5500 μm , and emission currents between 125,000 and 127,000 nA. The imaging process and evaluation used resolutions from 1 to 500 μm .

The SEM images were analyzed for fragments measured along two particle axes (perpendicular). In total, more than 2800 fragments were analyzed. The size distribution was first applied to the total weight loss of the experiments yielding a weight distribution in predefined size classes to calculate the increase in surface area. Next, the resulting weights were converted into a particle count and multiplied by the average surface area of a single particle in the respective size class.^{52–54} Finally, the thus determined surface areas were summed up and divided by the initial surface area of the 525 particles outputting the relative increase in surface area. The exact calculation steps are listed in the SI.

3. RESULTS

The tests were first evaluated in terms of mass. For this purpose, all particles were weighed every 30 days before and after the tests. The relative mass loss per plastic measured after 90 days (three runs) is listed in Table 2 as a function of the sediment grain size classes in the boxes.

Statistical evaluations of changes in relative mass loss as a function of the first, second, or third 30 day period revealed no correlation (H_0 = no correlation; p : 0.08–0.99) across all plastics. However, the results must be interpreted considering that they are based on three mass difference values per plastic

Table 2. Relative Mass Loss of Each Plastic Type after 90 Days as a Function of Sediment Grain Size

grain size [mm]	EPS	PE-HD	PET
0.25–0.50	47.04%	0.195%	1.006%
0.50–1.00	56.66%	0.279%	1.045%
1.00–2.00	53.23%	0.148%	1.219%

and grain size (with 515 particles on average). The overall weight loss range behaves following the NIS of the plastics (Table 1). In addition, the fragmentation of PET is more significant than indicated because sediment particles got stuck in some fragment holes of the particles, which could not be removed and thus reduced the measured mass loss. However, all PET particles were investigated for potential sediment incorporation, and the mass difference was added for the evaluation. Furthermore, the effect of PET entry into the sediment layer was observed during the tests but was hardly measurable due to lacking trackability. However, since this effect is also occurring in nature, it is not enhancing the fragmentation rate unrealistically.

However, the relative or absolute mass loss is an ambiguous unit. Since each plastic has different shapes, especially in the environment, laboratory values cannot be meaningfully classified using relative mass loss. A leading contributor to fragmentation is the irregular surface of a plastic object exposed to environmental influences. It is directly responsible for the amount of microplastic produced. Therefore, a unit that relates the mass loss (ML) to the surface area (SA) should be used. Compared to specifying the volume loss (VL) in relation to the SA, the ML per SA has the advantage that potential effects determined by the mass rather than volume, such as the leaching of additives, can be better approximated. For this reason, Table 3 shows the average ML per SA for all plastics as

Table 3. Average Mass Loss per Surface Area and Day for all Plastic Types Investigated as a Function of the Grain Size

grain size [mm]	EPS [mg/(m ² ·d)]	PE-HD [mg/(m ² ·d)]	PET [mg/(m ² ·d)]
0.25–0.50	114	11	66.5
0.50–1.00	141	16	69
1.00–2.00	136	8.5	80.6

the ratio of ML to SA and day. However, the ML per SA and VL per SA units can be converted into each other by including the respective plastic density (Table 1).

The surface area to volume ratio (SA/VR) is a crucial variable for different factors that can potentially damage microplastics. However, by measuring a mass loss or determining an ML per SA, a statement about the increase in surface area of the initial particle due to fragmentation is impossible. For this purpose, it is necessary to determine the average fragment size, shape, and, thus, surface area. The fragment's shape depends on the type of mechanical force acting on the plastic and can be estimated via several analysis methods, e.g., a scanning electron microscope (SEM).

Figure 6b shows a PE-HD plastic particle surface after 90 days in the Slosh-Box, exemplarily indicating the different damage mechanisms and adhering fragments versus an image of a virgin particle surface (Figure 6a). Flaking caused by shear stress can be seen at location 1. Position 2 shows a dragging site, identifiable through the length of the groove. An additional mechanical damage mechanism, impact fragmentation, can be seen at site 3. The resulting hole indicates a collision with a more rigid particle, probably a sediment grain. Similar damage mechanisms can be seen for PET.

In general, it can be observed that the surfaces of PET and PE-HD become rougher and more uneven with increasing stress duration (Figure 6b,f; Figure S11). However, EPS does not exhibit significant changes after the first 30 days, although

the mass loss, relative and absolute, is the greatest of all samples. However, EPS is also the only plastic with significant size change. While the volume loss per particle for PE-HD and PET is too small for a change visible to the naked eye, the average diameter of EPS particles changed from 4.5 to 3.5 mm after 90 days, corresponding to a volume loss of almost 53%. For each sediment grain size distribution used, the abrasion patterns caused by the sediment are comparable in characteristics for each 30 day period.

Since fragments (daughter fragments) remained on the parent particle surface after the experimental duration, a rough approximation of the average fragment size and its surface area is possible. Particles in the micron size range adhering to the surface, even after cleaning processes, were reported by Meides et al. (2022)⁵² as well. Thus, a fragment size distribution can be derived. However, the fragment size distribution evaluation is subject to the assumption that these particles on the plastics' surface are representative of all emerged fragments.⁵³ The SEM images with decreased magnification (100–500 μm) support this assumption since almost no fragments or surface damages are visible. Thus, the majority of fragments must be smaller than 100 μm .⁵⁴

The results of the SEM image evaluation are displayed as a size distribution graph in Figure 7. Generally, most daughter particles were observable in a size range from 0.1 to 1.0 μm . Since the SEM is a 2D imaging process, the particles cannot be described in all three dimensions and were assumed to be spherical for the calculations.

However, the calculated surface area most likely underestimates the actual increase in surface area due to the fragments' deviations from a spherical shape and overall surface roughness. The increase in surface area for each plastic is listed in Table 4.

4. DISCUSSION

The results prove that no UV radiation or other sources of plastic degrading influences are a premise for the fragmentation of virgin plastics, independent of their density. Furthermore, the experiments demonstrate that the minor mechanical impact of sediment is already sufficient for measurable mass loss, ergo, the generation of microplastics. In addition, the Slosh-Box presents a suitable test facility for the long-term simulation of the mechanical fragmentation influences at a shore environment (with modest wave action). The physical model thus poses the first concept environment, including all relevant drivers for the mechanical fragmentation of (micro)-plastics acting simultaneously. The results, however, are only valid for non-weathered virgin plastics.

The relevance of sediment for the fragmentation of plastics is well-known in the literature but finds little application in model experiments.³⁴ Their focus is usually on sufficiently strong UV weathering, through which fragmentation already occurs at minor mechanical impacts. However, the values determined in this way deviate from natural processes. Furthermore, the different blank tests, agitation without sediment, and stagnation exhibit a negligible fragmentation rate. It can therefore be assumed that the impact of the particles onto the boxes' walls has no significant influence on the fragmentation behavior. Thus, a model effect is not present in this respect. Furthermore, the blank tests showed that collisions between the particles are also not a decisive fragmentation factor. Consequently, sediment is necessary for

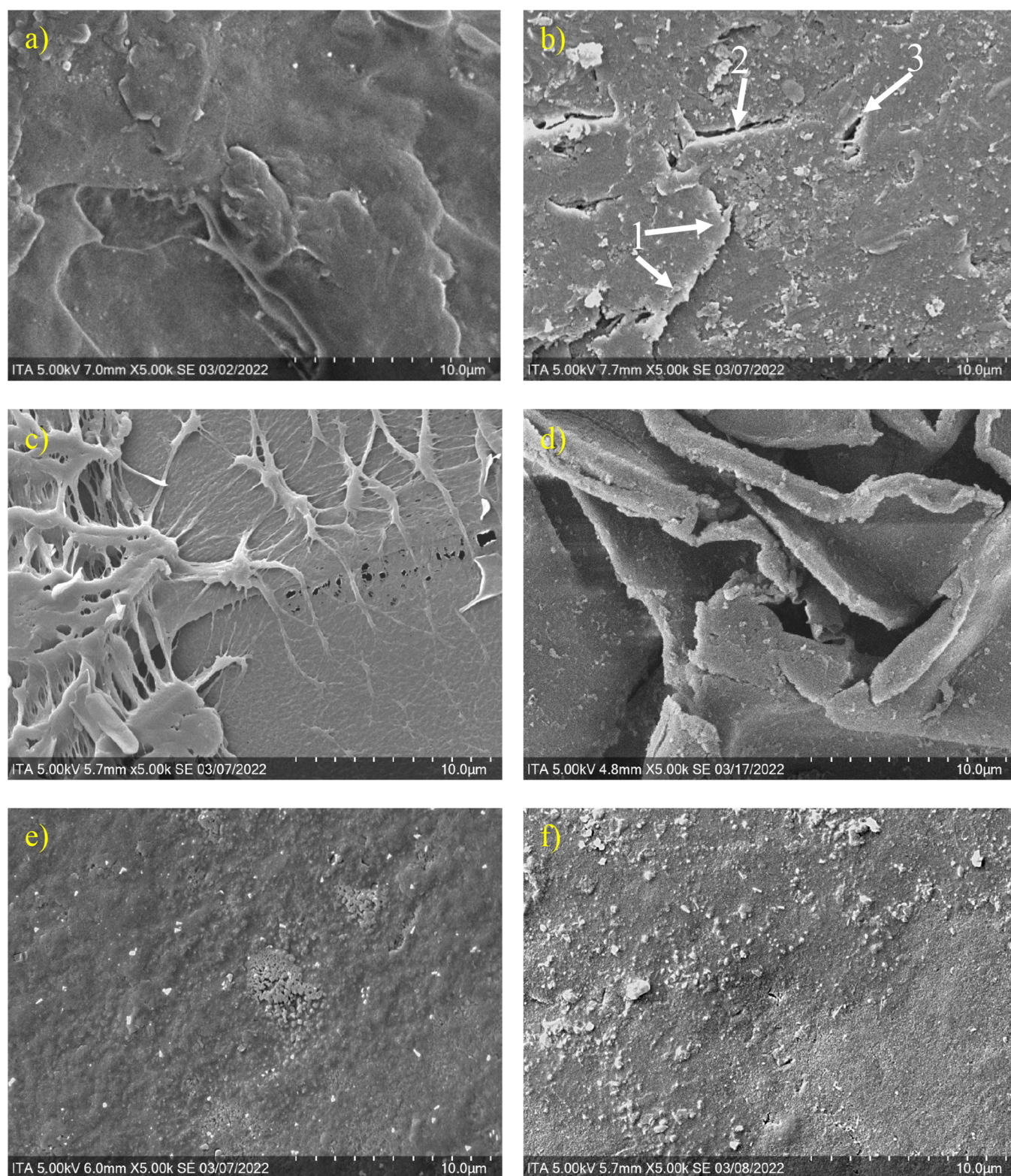


Figure 6. Virgin (a, c, e) and 90 day strained (b, d, f) particles. PE-HD (a, b), EPS (c, d), and PET (e, f), at a 10 μm resolution (SEM-imaging by ITA RWTH Aachen University).

modeling the fragmentation of plastics in coastal areas with moderate wave action.

The influence of the sediment grain size on the fragmentation rate is observable in Tables 2 and 3. Initially, the mass loss per plastic increases in parallel with grain size but decreases for the 1–2 mm sediment class for all buoyant

plastics tests. The increase can be attributed to the comparably high impulse due to the greater mass per sediment grain. However, the subsequent decrease in the fragmentation rate is caused by another effect. Increasing mass per grain reduces the sediment's lifting duration, thus colliding with the plastic particles less frequently. In addition, the increased fragmenta-

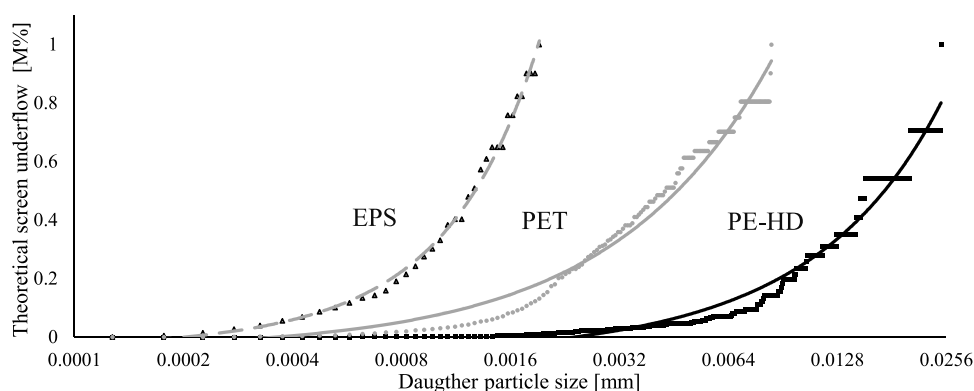


Figure 7. Particle size distributions of EPS (gray triangles), PE-HD (black squares), and PET (dark gray dots) daughter particles.

Table 4. Changes in Total Surface Area of 525 EPS, 525 PE-HD, and 525 PET Particles through Fragmentation

		EPS	PE-HD	PET
virgin particle SA	[cm ²]	334	313	198
total SA after 90 d	[cm ²]	793,587	556	1700
increase in SA	[<i>n</i> -fold]	2375	1	8.6

tion potential per grain is obviously not compensating for the reduction in collisions. This effect can be confirmed with the PET tests, where the fragmentation rate is highest at the largest grain size. Therefore, it can be concluded that a transfer of test results to nature is linked to the prevailing in situ conditions and the plastics' densities. On gravel beaches, for example, fragmentation of buoyant plastics will occur mainly during a storm, while on a sandy beach, buoyant plastics will fragment even at lower wave energy. For sinking particles, abrasion is present in both settings unless incorporated in (non-moving) sediment and shielded versus abrasion.⁷⁰ This conclusion agrees partly with studies by Efimova et al. (2018).⁵⁷

An additional significant aspect of this study is the particle size and composition used. While many studies in the fragmentation range of plastics operate with particle sizes in the micron range,^{52–54,71} granules with a diameter of around 5 mm were selected in the studies presented here. The particles in mentioned studies are usually generated by cryo-milling and, in contrast to the particles in this study, have a wide variety of fracture points and shapes. Thus, the results become difficult to compare or extrapolate due to several unknown crucial values, such as the total surface area of the particles used. Nevertheless, cryo-milling is used due to the acceleration of the relevant processes. This results from the increased surface-to-volume ratio, which allows for rapid fragmentation. However, this can only inadequately be used to infer the fragmentation of plastics with larger dimensions since these, in addition to a smaller total surface area per mass, exhibit different transport behavior and thus experience different stresses than smaller particles. Furthermore, since plastic waste at a shore is inhomogeneous in shape (often films⁵⁹), it will experience fragmenting influences in different ways. Thus, laboratory-determined fragmentation values will only apply to the investigated plastic shapes (and approximate densities). On the other hand, this would imply that laboratory experiments have to characterize the surface before conducting a fragmentation investigation. Neglecting this would lead to less valuable results since the fragmentation rate could not be related to the initial contact surface and other particle shape

parameters (e.g., size), which have proven crucial for plastic fragmentation.

This leads to the conclusion that the fragmentation of plastic particles increases exponentially over time since the generated fragments comminute more quickly due to the increased surface area. This aspect can be seen in the experiments employing the EPS fraction. While smaller, still visible fragments were present only to a limited extent, a film of EPS floated on the entire water surface, which was partly visible even on foam bubbles. This conclusion is supported by the particle size distribution in Figure 7 and the overall SEM image analysis. Both revealed that most particles were detectable in the micron and submicron size range, with most particles present in the smallest size class of 0.1–0.15 μm throughout all plastic types (which did not account for the most significant mass proportion, though). In addition, although the mass loss differed per sediment grain size class, the fragment size distribution remained roughly equal within each plastic type.

Nevertheless, it could also be possible that the prevailing forces were only sufficient to damage and extract a fragment in the (sub)micron size range since barely any larger particles were detected. However, this assumption can only be answered through increased sampling during the 90 day experimental period. Yet, even sampling every 30 days revealed no final answer to this question, evincing further investigation of the exact phenomenon of fragmentation on an individual particle's scale.

Generally, the results lead to the question of which influence is more relevant: fragmenting more mass per time from a particle or generating more surface area per time. Since these influences cannot be separated in a certain way, it depends on the respective scope, whether the focus is on a concentration or a defined particle size. Employing the results of Table 4, the massive increase in the surface area becomes evident. For EPS, the factor is above 2300, apparent by foam layers floating on the water surface after the experiments. However, even for PET's and PE-HD's relatively small total mass losses, the surface area increases between 1- and 8.6-fold. Thus, since the working surface area is a crucial factor for leaching and adhering processes, the idea of extrapolating these results onto the massive amounts of plastic waste in the ocean reveals the significance of this and further plastic fragmentation studies. In addition, the results are only applicable to the shapes and (virgin) plastics used. Other plastics and shapes, e.g., foils, with differing SV-ratios, would generate deviating fragment amounts.⁵⁹

While posing a new unique test environment incorporating several in other studies disregarded influences for fragmentation, the Slosh-Box represents a beach environment only to a limited extent. The limited, frequent, and constant wave energy and, thus, limited turbulences deviate from realistic wave patterns. Although purposely excluded, UV radiation and maybe even wet/dry cycles would improve the comparability. Additionally, the sediment used is not present at all beaches, reducing the results to beaches with comparable wave patterns and sediment. Nevertheless, to our knowledge, the Slosh-Box poses the approach including the highest amount of different mechanical fragmentation drivers.

The SEM results must be interpreted concerning the proportion of the images used to extrapolate the particle distribution compared to the whole particle surface. Whether this distribution describes the actual distribution of the daughter fragments on the parent particles' surface could only be determined with an overall SEM scan of several particles, requiring a well-working image analysis tool. However, this poses an enormous undertaking in terms of time and finances. A remedy to this problem is a particle counter, detecting particles in all size ranges in the water used in the experiments. However, this counter can only be used if no interfering particles like sediment or crystalline salt of the same size are present since these would heavily influence the particle count.

In addition, smaller particles than detected were probably present in the experiments after 30, 60, or 90 days but did not cling to the surface or were too small for the utilized resolutions. Thus, they were hardly detectable and out of the microplastic definition used in this study. In addition, contamination throughout the experiments by, e.g., plastic particles from sediment packaging or the box' wall, cannot be excluded by 100%.

Future studies tying in with this research should maintain comparable mechanical wear and include sediment if a transfer into nature is desired. In addition, in combination with mechanical wear and its synergetic effects, UV radiation should be further investigated since no studies to date have included long-term tests with wave action, sediment, salt water, and UV radiation acting concurrently. Finally, variations in investigated plastic shapes (1-D and 2-D objects) should be included.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.3c02189>.

Calculation steps for surface area increase; additional SEM images (PDF)

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■ REFERENCES

- (1) Hidalgo-Ruz, V.; Gutow, L.; Thompson, R. C.; Thiel, M. Microplastics in the marine environment: a review of the methods used for identification and quantification. *Environ. Sci. Technol.* **2012**, *46*, 3060–3075.
- (2) Burns, E. E.; Boxall, A. B. A. Microplastics in the aquatic environment: Evidence for or against adverse impacts and major knowledge gaps. *Environ. Toxicol. Chem.* **2018**, *37*, 2776–2796.
- (3) Hartmann, N. B.; Hüffer, T.; Thompson, R. C.; Hassellöv, M.; Verschoor, A.; Dagaard, A. E.; Rist, S.; Karlsson, T.; Brennholt, N.; Cole, M.; et al. Are We Speaking the Same Language? Recommendations for a Definition and Categorization Framework for Plastic Debris. *Environ. Sci. Technol.* **2019**, *53*, 1039–1047.
- (4) Ma, H.; Pu, S.; Liu, S.; Bai, Y.; Mandal, S.; Xing, B. Microplastics in aquatic environments: Toxicity to trigger ecological consequences. *Environ. Pollut.* **2020**, *261*, No. 114089.
- (5) Bakir, A.; Rowland, S. J.; Thompson, R. C. Enhanced desorption of persistent organic pollutants from microplastics under simulated physiological conditions. *Environ. Pollut.* **2014**, *185*, 16–23.
- (6) Auta, H. S.; Emenike, C. U.; Fauziah, S. H. Distribution and importance of microplastics in the marine environment: A review of the sources, fate, effects, and potential solutions. *Environ. Int.* **2017**, *102*, 165–176.
- (7) Yu, Q.; Hu, X.; Yang, B.; Zhang, G.; Wang, J.; Ling, W. Distribution, abundance and risks of microplastics in the environment. *Chemosphere* **2020**, *249*, No. 126059.
- (8) Xu, S.; Ma, J.; Ji, R.; Pan, K.; Miao, A.-J. Microplastics in aquatic environments: Occurrence, accumulation, and biological effects. *Sci. Total Environ.* **2020**, *703*, No. 134699.
- (9) Rochman, C. M. The Complex Mixture, Fate and Toxicity of Chemicals Associated with Plastic Debris in the Marine Environment. In *Marine Anthropogenic Litter*; Bergmann, M.; Gutow, L.; Klages, M., Eds.; Springer International Publishing: Cham, 2015; pp. 117–140, DOI: [10.1007/978-3-319-16510-3_5](https://doi.org/10.1007/978-3-319-16510-3_5).
- (10) Bakir, A.; O'Connor, I. A.; Rowland, S. J.; Hendriks, A. J.; Thompson, R. C. Relative importance of microplastics as a pathway for the transfer of hydrophobic organic chemicals to marine life. *Environ. Pollut.* **2016**, *219*, 56–65.
- (11) Camacho, M.; Herrera, A.; Gómez, M.; Acosta-Dacal, A.; Martínez, I.; Henríquez-Hernández, L. A.; Luzardo, O. P. Organic pollutants in marine plastic debris from Canary Islands beaches. *Sci. Total Environ.* **2019**, *662*, 22–31.
- (12) Pozo, K.; Urbina, W.; Gómez, V.; Torres, M.; Nuñez, D.; Příbylová, P.; Audy, O.; Clarke, B.; Arias, A.; Tombesi, N.; et al. Persistent organic pollutants sorbed in plastic resin pellet - "Nurdles" from coastal areas of Central Chile. *Mar. Pollut. Bull.* **2020**, *151*, No. 110786.

- (13) Yu, Y.; Ma, R.; Qu, H.; Zuo, Y.; Yu, Z.; Hu, G.; Li, Z.; Chen, H.; Lin, B.; Wang, B.; et al. Enhanced adsorption of tetrabromobisphenol A (TBBPA) on cosmetic-derived plastic microbeads and combined effects on zebrafish. *Chemosphere* **2020**, *248*, No. 126067.
- (14) Setälä, O.; Fleming-Lehtinen, V.; Lehtiniemi, M. Ingestion and transfer of microplastics in the planktonic food web. *Environ. Pollut.* **2014**, *185*, 77–83.
- (15) Elizalde-Velázquez, A.; Carcano, A. M.; Crago, J.; Green, M. J.; Shah, S. A.; Cañas-Carrell, J. E. Translocation, trophic transfer, accumulation and depuration of polystyrene microplastics in *Daphnia magna* and *Pimephales promelas*. *Environ. Pollut.* **2020**, *259*, No. 113937.
- (16) Cózar, A.; Echevarría, F.; González-Gordillo, J. I.; Irigoien, X.; Úbeda, B.; Hernández-León, S.; Palma, Á. T.; Navarro, S.; García-de-Lomas, J.; Ruiz, A.; et al. Plastic debris in the open ocean. *Proc. Natl. Acad. Sci. U. S. A.* **2014**, *111*, 10239–10244.
- (17) Geyer, R.; Jambeck, J. R.; Law, K. L. Production, use, and fate of all plastics ever made. *Sci. Adv.* **2017**, *3*, No. e1700782.
- (18) Janssens, V. *Plastics - The Facts 2022*; Plastics Europe: Brussels, Belgium, 2022.
- (19) Beer, S.; Garm, A.; Huwer, B.; Dierking, J.; Nielsen, T. G. No increase in marine microplastic concentration over the last three decades - A case study from the Baltic Sea. *Sci. Total Environ.* **2018**, *621*, 1272–1279.
- (20) Pabortsava, K.; Lampitt, R. S. High concentrations of plastic hidden beneath the surface of the Atlantic Ocean. *Nat. Commun.* **2020**, *11*, 4073.
- (21) Law, K. L.; Morét-Ferguson, S.; Maximenko, N. A.; Proskurowski, G.; Peacock, E. E.; Hafner, J.; Reddy, C. M. Plastic accumulation in the North Atlantic subtropical gyre. *Science* **2010**, *329*, 1185–1188.
- (22) Lebreton, L.; Egger, M.; Slat, B. A global mass budget for positively buoyant macroplastic debris in the ocean. *Sci. Rep.* **2019**, *9*, 12922.
- (23) Niaounakis, M. Degradation of Plastics in the Marine Environment. In *Management of Marine Plastic Debris*; 1st ed.; Elsevier, Ed.; Elsevier: Amsterdam, 2017; pp. 127–142, DOI: 10.1016/B978-0-323-44354-8.00003-3.
- (24) Koelmans, A. A.; Redondo-Hasselerharm, P. E.; Nor, N. H. M.; de Ruijter, V. N.; Mintenig, S. M.; Kooi, M. Risk assessment of microplastic particles. *Nat. Rev. Mater.* **2022**, *7*, 138–152.
- (25) Ho, N. H. E.; Not, C. Selective accumulation of plastic debris at the breaking wave area of coastal waters. *Environ. Pollut.* **2019**, *245*, 702–710.
- (26) van Sebille, E.; Aliani, S.; Law, K. L.; Maximenko, N.; Alsina, J. M.; Bagaev, A.; Bergmann, M.; Chapron, B.; Chubarenko, I.; Cózar, A.; et al. The physical oceanography of the transport of floating marine debris. *Environ. Res. Lett.* **2020**, *15*, 23003.
- (27) van Cauwenberghe, L.; Vanreusel, A.; Mees, J.; Janssen, C. R. Microplastic pollution in deep-sea sediments. *Environ. Pollut.* **2013**, *182*, 495–499.
- (28) Woodall, L. C.; Sanchez-Vidal, A.; Canals, M.; Paterson, G. L. J.; Coppock, R.; Sleight, V.; Calafat, A.; Rogers, A. D.; Narayanaswamy, B. E.; Thompson, R. C. The deep sea is a major sink for microplastic debris. *R. Soc. Open Sci.* **2014**, *1*, No. 140317.
- (29) Corcoran, P. L. Benthic plastic debris in marine and fresh water environments. *Environ. Sci.: Processes Impacts* **2015**, *17*, 1363–1369.
- (30) Kane, I. A.; Clare, M. A. Dispersion, Accumulation, and the Ultimate Fate of Microplastics in Deep-Marine Environments: A Review and Future Directions. *Front. Earth Sci.* **2019**, *7*.
- (31) Kooi, M.; van Nes, E. H.; Scheffer, M.; Koelmans, A. A. Ups and Downs in the Ocean: Effects of Biofouling on Vertical Transport of Microplastics. *Environ. Sci. Technol.* **2017**, *51*, 7963–7971.
- (32) Corcoran, P. L.; Biesinger, M. C.; Grifi, M. Plastics and beaches: a degrading relationship. *Mar. Pollut. Bull.* **2009**, *58*, 80–84.
- (33) Brandon, J.; Goldstein, M.; Ohman, M. D. Long-term aging and degradation of microplastic particles: Comparing in situ oceanic and experimental weathering patterns. *Mar. Pollut. Bull.* **2016**, *110*, 299–308.
- (34) Born, M. P.; Brüll, C. From model to nature - A review on the transferability of marine (micro-) plastic fragmentation studies. *Sci. Total Environ.* **2022**, *811*, No. 151389.
- (35) Corcoran, P. L. Degradation of Microplastics in the Environment. In *Handbook of Microplastics in the Environment*; Rocha-Santos, T.; Costa, M.; Mouneyrac, C., Eds.; Springer International Publishing: Cham, 2020; pp. 1–12.
- (36) Lin, W.; Jiang, R.; Xiao, X.; Wu, J.; Wei, S.; Liu, Y.; Muir, D. C. G.; Ouyang, G. Joint effect of nanoplastics and humic acid on the uptake of PAHs for *Daphnia magna*: A model study. *J. Hazard. Mater.* **2020**, *391*, No. 122195.
- (37) Hahladakis, J. N.; Velis, C. A.; Weber, R.; Iacovidou, E.; Purnell, P. An overview of chemical additives present in plastics: Migration, release, fate and environmental impact during their use, disposal and recycling. *J. Hazard. Mater.* **2018**, *344*, 179–199.
- (38) Khaled, A.; Rivaton, A.; Richard, C.; Jaber, F.; Sleiman, M. Phototransformation of Plastic Containing Brominated Flame Retardants: Enhanced Fragmentation and Release of Photoproducts to Water and Air. *Environ. Sci. Technol.* **2018**, *52*, 11123–11131.
- (39) Wilson, S. *AMAP Assessment 2016: Chemicals of Emerging Arctic Concern*; Arctic Monitoring and Assessment Programme: Oslo, NOR, 2018.
- (40) Colom, X.; Cañavate, J.; Suñol, J. J.; Pagès, P.; Saurina, J.; Carrasco, F. Natural and artificial aging of polypropylene–polyethylene copolymers. *J. Appl. Polym. Sci.* **2003**, *87*, 1685–1692.
- (41) Lambert, S.; Sinclair, C.; Boxall, A. Occurrence, degradation, and effect of polymer-based materials in the environment. *Rev. Environ. Contam. Toxicol.* **2014**, *227*, 1–53.
- (42) Lambert, S.; Wagner, M. Formation of microscopic particles during the degradation of different polymers. *Chemosphere* **2016**, *161*, 510–517.
- (43) Andrady, A. L. The plastic in microplastics: A review. *Mar. Pollut. Bull.* **2017**, *119*, 12–22.
- (44) Song, Y. K.; Hong, S. H.; Jang, M.; Han, G. M.; Jung, S. W.; Shim, W. J. Combined Effects of UV Exposure Duration and Mechanical Abrasion on Microplastic Fragmentation by Polymer Type. *Environ. Sci. Technol.* **2017**, *51*, 4368–4376.
- (45) Cai, L.; Wang, J.; Peng, J.; Wu, Z.; Tan, X. Observation of the degradation of three types of plastic pellets exposed to UV irradiation in three different environments. *Sci. Total Environ.* **2018**, *628*–629, 740–747.
- (46) Klein, S.; Dimzon, I. K.; Eubeler, J.; Knepper, T. P. Analysis, Occurrence, and Degradation of Microplastics in the Aqueous Environment. In *Freshwater Microplastics*; Wagner, M.; Lambert, S., Eds.; The Handbook of Environmental Chemistry; Springer International Publishing: Cham, 2018; pp. 51–67.
- (47) Ranjan, V. P.; Goel, S. Degradation of Low-Density Polyethylene Film Exposed to UV Radiation in Four Environments. *J. Hazard. Toxic Radioact. Waste* **2019**, *23*, No. 4019015.
- (48) Julienne, F.; Delorme, N.; Lagarde, F. From macroplastics to microplastics: Role of water in the fragmentation of polyethylene. *Chemosphere* **2019**, *236*, No. 124409.
- (49) Julienne, F.; Lagarde, F.; Delorme, N. Influence of the crystalline structure on the fragmentation of weathered polyolefines. *Polym. Degrad. Stab.* **2019**, *170*, No. 109012.
- (50) Andrady, A. L. Microplastics in the marine environment. *Mar. Pollut. Bull.* **2011**, *62*, 1596–1605.
- (51) Zhu, L.; Zhao, S.; Bittar, T. B.; Stubbins, A.; Li, D. Photochemical dissolution of buoyant microplastics to dissolved organic carbon: Rates and microbial impacts. *J. Hazard. Mater.* **2020**, *383*, No. 121065.
- (52) Meides, N.; Mauel, A.; Menzel, T.; Altstädt, V.; Ruckdäschel, H.; Senker, J.; Strohmriegel, P. Quantifying the fragmentation of polypropylene upon exposure to accelerated weathering. *Microplast. Nanoplast.* **2022**, *2*, 23.
- (53) Meides, N.; Menzel, T.; Poetzschner, B.; Löder, M. G. J.; Mansfeld, U.; Strohmriegel, P.; Altstaedt, V.; Senker, J. Reconstructing the Environmental Degradation of Polystyrene by Accelerated Weathering. *Environ. Sci. Technol.* **2021**, *55*, 7930–7938.

- (54) Menzel, T.; Meides, N.; Mauel, A.; Mansfeld, U.; Kretschmer, W.; Kuhn, M.; Herzig, E. M.; Altstädt, V.; Strohriegel, P.; Senker, J.; et al. Degradation of low-density polyethylene to nanoplastic particles by accelerated weathering. *Sci. Total Environ.* **2022**, 826, No. 154035.
- (55) Hinata, H.; Sagawa, N.; Kataoka, T.; Takeoka, H. Numerical modeling of the beach process of marine plastics: A probabilistic and diagnostic approach with a particle tracking method. *Mar. Pollut. Bull.* **2020**, 152, No. 110910.
- (56) Dring, M. J.; Wagner, A.; Franklin, L. A.; Kuhlenskamp, R.; Lüning, K. Seasonal and diurnal variations in ultraviolet-B and ultraviolet-A irradiances at and below the sea surface at Helgoland (North Sea) over a 6-year period. *Helgol. Mar. Res.* **2001**, 55, 3–11.
- (57) Efimova, I.; Bagaeva, M.; Bagaev, A.; Kilesa, A.; Chubarenko, I. P. Secondary Microplastics Generation in the Sea Swash Zone With Coarse Bottom Sediments: Laboratory Experiments. *Front. Mar. Sci.* **2018**, 5, 313.
- (58) Chubarenko, I.; Efimova, I.; Bagaeva, M.; Bagaev, A.; Isachenko, I. On mechanical fragmentation of single-use plastics in the sea swash zone with different types of bottom sediments: Insights from laboratory experiments. *Mar. Pollut. Bull.* **2020**, 150, No. 110726.
- (59) Kalogerakis, N.; Karkanorachaki, K.; Kalogerakis, G. C.; Triantafyllidi, E. I.; Gotsis, A. D.; Partsinevelos, P.; Fava, F. Microplastics Generation: Onset of Fragmentation of Polyethylene Films in Marine Environment Mesocosms. *Front. Mar. Sci.* **2017**, 4, 84.
- (60) Bond, T.; Ferrandiz-Mas, V.; Felipe-Sotelo, M.; van Seville, E. The occurrence and degradation of aquatic plastic litter based on polymer physicochemical properties: A review. *Crit. Rev. Environ. Sci. Technol.* **2018**, 48, 685–722.
- (61) Erni-Cassola, G.; Zadjelovic, V.; Gibson, M. I.; Christie-Oleza, J. A. Distribution of plastic polymer types in the marine environment; A meta-analysis. *J. Hazard. Mater.* **2019**, 369, 691–698.
- (62) Nelms, S. E.; Eyles, L.; Godley, B. J.; Richardson, P. B.; Selley, H.; Solandt, J.-L.; Witt, M. J. Investigating the distribution and regional occurrence of anthropogenic litter in English marine protected areas using 25 years of citizen-science beach clean data. *Environ. Pollut.* **2020**, 263, No. 114365.
- (63) Chubarenko, I.; Stepanova, N. Microplastics in sea coastal zone: Lessons learned from the Baltic amber. *Environ. Pollut.* **2017**, 224, 243–254, DOI: 10.1016/j.envpol.2017.01.085.
- (64) van Rijn, L. C. Unified View of Sediment Transport by Currents and Waves. I: Initiation of Motion, Bed Roughness, and Bed-Load Transport. *J. Hydraul. Eng.* **2007**, 133, 649–667.
- (65) Gewert, B.; Plassmann, M.; Sandblom, O.; MacLeod, M. Identification of Chain Scission Products Released to Water by Plastic Exposed to Ultraviolet Light. *Environ. Sci. Technol. Lett.* **2018**, 5, 272–276.
- (66) DIN Deutsches Institut für Normung e. V., DIN German Institute for Standardization. *Plastics - Methods for determining the density of non-cellular plastics: Part 1: Immersion method, liquid pycnometer method and titration method (ISO 1183-1:2019, Corrected version 2019-05); German version EN ISO 1183-1:2019*; Beuth: Berlin, 2019, 83.080.01 (1183-1:2019-09) (accessed 3rd June 2022).
- (67) Fazey, F. M. C.; Ryan, P. G. Biofouling on buoyant marine plastics: An experimental study into the effect of size on surface longevity. *Environ. Pollut.* **2016**, 210, 354–360, DOI: 10.1016/j.envpol.2016.01.026.
- (68) Kaiser, D.; Kowalski, N.; Waniek, J. J. Effects of biofouling on the sinking behavior of microplastics. *Environ. Res. Lett.* **2017**, 12, No. 124003.
- (69) Harrison, J. P.; Hoellein, T. J.; Sapp, M.; Tagg, A. S.; Ju-Nam, Y.; Ojeda, J. J. Microplastic-Associated Biofilms: A Comparison of Freshwater and Marine Environments. In *Freshwater Microplastics*; Wagner, M.; Lambert, S., Eds.; The Handbook of Environmental Chemistry; Springer International Publishing: Cham, 2018; pp. 181–201.
- (70) Chubarenko, I.; Esiukova, E.; Bagaev, A.; Isachenko, I.; Demchenko, N.; Zobkov, M.; Efimova, I.; Bagaeva, M.; Khatmullina, L. Behavior of Microplastics in Coastal Zones. *Microplastic Contamination in Aquatic Environments*; Elsevier, 2018, 175–223, DOI: 10.1016/B978-0-12-813747-5.00006-0.
- (71) Bråte, I. L. N.; Blázquez, M.; Brooks, S. J.; Thomas, K. V. Weathering impacts the uptake of polyethylene microparticles from toothpaste in Mediterranean mussels (*M. galloprovincialis*). *Sci. Total Environ.* **2018**, 626, 1310–1318.