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Foamed Polystyrene in the Marine Environment: Sources, Additives, Transport, Behavior, and Impacts

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14 **Abstract**

15 Foamed polystyrene (PS) that may be either expanded (EPS) or extruded (XPS) is a rigid, lightweight
16 insulating thermoplastic that has a variety of uses in the consumer, packaging, construction, and
17 marine sectors. The properties of the material also result in waste that is readily generated,
18 dispersed, and fragmented in the environment. This review focuses on foamed PS in the marine
19 setting, including its sources, transport, degradation, acquisition of contaminants, ingestion by
20 animals, and biological impacts arising from the mobilization of chemical additives. In the ocean,
21 foamed PS is subject to wind-assisted transport and fracturing via photolytic degradation. The
22 material may also act as a substrate for rafting organisms while being exposed to elevated
23 concentrations of natural and anthropogenic surface-active chemicals in the sea surface microlayer.
24 In the littoral setting, fragmentation is accentuated by milling in the swash zone and abrasion when
25 beached, with wind transport leading to the temporary burial of significant quantities of material.
26 Ingestion of EPS and XPS has been documented for a variety of marine animals, but principally those
27 that feed at the sea surface or use the material as a habitat. As well as risking injuries due to gastro-
28 intestinal blockage, ingestion of foamed PS exposes animals to harmful chemicals, and of greatest
29 concern in this respect is the presence of the historical, but still recycled, flame-retardant,
30 hexabromocyclododecane. Because foamed PS is particularly difficult to retrieve as a constituent of
31 marine litter, means of reducing its presence and impacts will rely on the elimination of processes
32 that generate foamed waste, modification of current storage and disposal practices, and the
33 development of more durable and sustainable alternatives.

34

35

36 **1. Introduction**

37 Marine pollution from plastics has received an enormous amount of scientific, media, and public
38 attention over the past two decades. Studies on plastics have focused on methods of sampling,
39 sources, distributions, impacts on the environment and on wildlife, and the uptake of pollutants,
40 with a number of reviews that attempt to synthesize research in each area or a combination of areas
41 (1-4). For materials of comparable bulk characteristics (e.g. size, density, and crystallinity),
42 distributions, sinks, and physical impacts are expected to be broadly similar and in most review
43 articles plastics or microplastics are explicitly or implicitly defined under a single umbrella. For
44 foamed plastics, however, densities are so much lower than unfoamed equivalents that their
45 behavior is distinctly different and they should, strictly, be classified independently.

46 In the present paper, the focus is on one of the most important and widely used types of foamed
47 plastic, polystyrene (PS). This material is a common component of marine litter and is particularly
48 problematic from both a local and transboundary perspective (5-9). Information and data are
49 critically reviewed in the scientific literature on the sources, chemical composition, transport, fate,
50 and impacts of foamed PS in the marine environment. Where informative, comparisons are also
51 made with (unfoamed) polyethylene, another common component of marine litter whose greater
52 density ensures its pathways and behavior are markedly different from foamed PS. The more general
53 challenges associated with the generation and disposal of large quantities of foamed PS in society
54 are addressed, and current and proposed solutions to these problems are reviewed.

55

56 **2. Foamed PS: Production, uses, waste, and marine littering**

57 PS is a rigid, amorphous thermoplastic produced by free radical vinyl polymerization of styrene. The
58 structure of the polymer can be written thus: $[\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)]_n$; where C_6H_5 is a pendant phenyl group
59 which restricts rotation and is responsible for many of the physical and mechanical properties of the
60 polymer. Both expanded PS (EPS) and extruded PS (XPS) are forms of the polymer that contain a high
61 proportion of air (> 95%) (10, 11). EPS is produced when the raw, pelletized material is expanded by
62 heating with steam to form cellular beads. Dried particles are then fused under steam and molded
63 into blocks or other shapes, with beads of 2 to 5 mm in diameter clearly visible in the final product.
64 The air within and between the beads gives EPS its insulating properties but inter-particle air, as
65 irregular gaps or voids, renders the material susceptible to (limited) water absorption. XPS is formed
66 when PS crystals, additives, and blowing agents are extruded at high temperature to produce a
67 frothy liquid that is subsequently shaped in a die as it cools and expands. XPS consists of tightly

68 packed cells that have no gaps or voids between them. This closed structure inhibits water
69 absorption and results in a smoother surface and a higher density than EPS. Note that Styrofoam® is
70 often used synonymously with foamed PS but is, strictly, a trademarked brand of XPS produced for
71 building insulation by Dow Chemical.

72 Foamed PS is commonly employed in home and appliance insulation, protective packaging,
73 automobile parts, embankment filling, lightweight concrete (as an aggregate), and food packaging
74 (11;12); with regard to the construction sector, XPS is favored over EPS where pressure, stability,
75 and humidity are especially high (13). The durability, low density, and insulating properties of
76 foamed PS have also resulted in many applications in the marine sector. Here, EPS (and less
77 frequently, XPS) are used in fish boxes, buoys, pontoons, floating docks, net floats, life jackets,
78 surfboards, and boat stands (14-17). As a tethered floating base, EPS is used directly, or for greater
79 durability, may be coated or covered by hard plastic or cement (13).

80 Because of its growing demand and extensive on land and at sea, coupled with recycling that is
81 constrained by its bulk and contamination (by food, for example), foamed PS represents an
82 important form of waste. European data for 2016/2017 suggest that waste generation of foamed PS
83 from construction and packaging was about 530,000 tonnes, with a recycling rate of 27% in total for
84 EPS (and 34% for single use packaging waste and 8% for construction waste) and energy recovery by
85 incineration as the most common method for its disposal (13).

86 Loss of foamed PS to the environment may occur via the transport, storage, or cutting of
87 construction material, escapement of waste from controlled and historical landfill, storage or
88 compaction of waste before or during disposal or recycling, deterioration or loss of structures in situ,
89 and littering and fly tipping. Waste enters the marine environment through rivers, stormwater, and
90 wastewater treatment plants, and from direct littering and loss or structural damage at sea or in the
91 littoral zone. Not only is foamed PS a significant contributor to marine litter worldwide (9;18-24), its
92 lightness and low density, ready transportation by the wind, and propensity to readily fragment
93 ensure that it disperses more widely and rapidly than other forms of (unfoamed) plastic, both at sea
94 and when beached (8;25;26). With small fragments readily blown around by the wind when dry and
95 adhering to surfaces when wet, foamed PS is also particularly difficult to retrieve during beach
96 cleans.

97 The images in Figure 1 exemplify some of the uses of foamed PS that may directly impact on the
98 marine environment, along with the volume, nature, and consequences of secondary (fragmented)
99 particles that can be readily washed up and blown around. Material illustrated here ranges in size
100 from EPS beads of a few mm in diameter to slabs greater than 1 m across. However, empirical

101 studies suggest that, ultimately, weathering may produce spherical and elongated particles of
102 dimensions down to hundreds of nm (27).

103

104 **3. Transport and physical behavior in the marine environment**

105 The properties of foamed PS that are of relevance to its behavior and fate in the marine
106 environment are shown in Table 1. Here, data are indicative and are based on the properties of a
107 specific brand or a range of brands of EPS, which is far better characterized than XPS in the
108 literature. Note, however, that in general, XPS has a slightly higher density, greater tensile, impact,
109 and compressive strengths, and lower water absorption than EPS (28).

110

111 *3.1. In the ocean*

112 The following discussion focuses on floating and fragmented foamed PS in the ocean, with the
113 effects and forcing mechanisms acting upon this type of litter conceptualized in Figure 2 as an aid to
114 the narrative.

115 One of the key differences in the transport plastics having a density slightly lower than seawater (like
116 polyethylene without any inclusions of air) to those having a density significantly lower than
117 seawater and floating at the surface (foamed plastics) is the influence of windage, or drift due to
118 wind forces (31). Specifically, and neglecting any phenomena incurred by viscous forces, wind
119 pressure acting on the upper ('sail') surface of a particle is opposed by the drag force applied to its
120 lower, submerged ('drag') surface, with the ratio of sail and drag surface areas dependent on particle
121 and fluid densities and determining the magnitude of windage. The high buoyancy of foamed PS also
122 confers a relatively low floating stability, especially if objects are rounded. Thus, because the center
123 of gravity is well above the sea surface, objects tend to repeatedly change position and orientation
124 during transportation (33).

125 The effect of windage on the ocean transport of foamed PS of density = 0.05 g cm^{-3} and polyethylene
126 of density = 0.95 g cm^{-3} was considered theoretically by Chubarenko et al. (32). Specifically,
127 calculations were performed for spherical particles (of any diameter) carried in inviscid (Baltic)
128 seawater of density $\sim 1.01 \text{ g cm}^{-3}$ and with a current speed, v_c , of 0.3 m s^{-1} that were subject to a
129 wind blowing in the same direction at a speed, v_w , of 10 m s^{-1} . The drift speeds for PS and
130 polyethylene, v_{PS} and v_{PE} , were estimated to be about 1.2 m s^{-1} and 0.4 m s^{-1} , respectively, or four
131 times and 25% higher than v_c . In other words, and under these environmental conditions, foamed PS

132 whose density is not significantly modified by fouling (see below) is predicted to travel three times
133 faster in seawater than polyethylene.

134 An additional consequence of foamed PS residing at the sea surface is that it is exposed to a greater
135 amount of sunlight than plastics that are less buoyant and, through turbulence, are transported in
136 the bulk medium (34). Moreover, the aromatic backbone of PS acts as effective absorber of solar
137 radiation in the ultraviolet (UV) region (35). Absorption of sunlight causes cleavage of polymer
138 chains by chain scission, with styrene monomers the principal product of degradation (36). Resulting
139 embrittlement of the foamed PS surface causes fracturing and, eventually, fragmentation (8).
140 Experiments performed by Song et al. (37) showed that two months of exposure to UV light
141 generated by a metal-halide lamp was sufficient to break EPS beads ($\sim 20 \text{ mm}^3$) into microfragments,
142 thereby exposing new surfaces to UV radiation and promoting further degradation. A recent study
143 conducted by Zhu et al. (38) compared the degradation of post-consumer EPS under simulated solar
144 radiation with that of other plastics (including polyethylene). Based on mass loss over the
145 experimental period employed, the authors estimated lifetimes of 2.7 years for EPS and 33 years for
146 polyethylene. By comparison, microbial biodegradation of foamed PS can be considered almost
147 negligible over such timeframes (39).

148

149 *3.2. In the littoral zone*

150 Ultimately, a significant fraction of both oceanic and land-derived foamed PS will end up in the
151 littoral zone, including mangroves, beaches, and rocky shores (19;20;24). The effects and forcing
152 mechanisms acting upon this type of litter on a sandy shoreline are conceptualized in Figure 3 as an
153 aid to the following discussion.

154 When beached, both photolytic and thermal degradation of foamed PS are accentuated because
155 significantly higher temperatures are possible in sand compared with seawater (8). Moreover,
156 mechanical fragmentation is highly favorable here because wind-driven transport engenders
157 frictional forces and collisional impacts on material of inherently low tensile strength (Table 1). For
158 example, experiments that exposed EPS beads to UV radiation under a metal-halide lamp for twelve
159 months and subsequently subjected them to mechanical abrasion (through agitation with sand)
160 resulted in the majority of the original particle volume becoming fragmented to sizes too small (< 1
161 μm) to be detected (37;40).

162 Mechanical fragmentation of foamed PS also takes place in the swash zone where litter already
163 weakened by photolytic processes is “milled” with sand and pebbles as it is transported under

164 dynamic, asymmetrical wave motion. Chubarenko and co-workers (41;42) conducted experiments in
165 which plastics, including EPS, were subject to simulated swash conditions for 24 h in the presence of
166 sand, gravel, and pebbles. Results revealed that material was smoothed, polished, torn, and
167 fragmented into beads and that, although impaction of EPS with pebbles was low compared with
168 other plastics because of the high buoyancy of the material, these interactions resulted in the
169 greatest number of fragmented particles. Significantly, despite the low density of EPS, some beads
170 formed on fragmentation became attached to or trapped-buried by the sediment. The burial and
171 subsequent compaction of EPS beads also appears to take place on more landward reaches of a
172 beach. Here, material blown against a physical barrier along with other light plastics is subsequently
173 buried by accumulations of drifting sand.

174

175 **4. Composition and chemical modification of foamed PS in the marine environment**

176 Although the general behavior of foamed PS in the oceans and when beached has been addressed
177 above, the precise impacts of the material in the marine setting are likely to be influenced by the
178 presence, concentrations, and mobilities of the monomer (styrene), oligomers, reaction residues,
179 and additives in the matrix, and any chemicals and contaminants that have been acquired from the
180 environment.

181 Residues in foamed PS include Fe_2O_3 , used as a catalyst in the production of styrene (43), and Zn
182 stearate, often used to ensure uniform cell nucleation in the production of EPS (44). Additives are
183 sometimes applied as a thin surface finish for protection but most are usually blended or molded
184 into the raw material to ensure uniform concentration and are tailored to the specific requirements
185 and applications of the material. For instance, addition of graphite can improve insulation properties
186 of construction boards, various pigments may be employed to impart a range of different colors, and
187 TiO_2 may be added to assist bacterial decomposition or as a pigment to provide a high refractive
188 index (13;45). Plasticizers and biocides are not generally used in foamed PS but the stabilizer and
189 antioxidant tris(4-nonylphenyl) phosphite, a source of the endocrine-disrupting nonylphenols, is
190 sometimes added (46). Traces of other organic additives in EPS have also been mentioned or implied
191 but have not been identified (47;48). However, because of the inherent flammability of foamed PS
192 the most commonly employed additives are flame-retardants.

193 *4.1. Hexabromocyclododecane*

194 Flame-retardants are added to foamed PS destined for the construction industry but are also
195 encountered in packaging material because one grade of material may be adopted for all production

196 (13). The most important flame-retardant used in EPS and XPS since the 1980s has been 1,2,5,6,9,10-
197 hexabromocyclododecane (HBCD) (49;50;51), whose physical, chemical, environmental, and
198 toxicological properties that are relevance to the discussion are given in Table S1. HBCD is added at
199 concentrations that are low relative to those of other halogenated compounds used to flame-retard
200 plastics; specifically, typical HBCD concentrations range from about 0.7 to 2.5% by weight of the raw
201 product, with XPS usually containing more of the retardant than EPS (52). Moreover, and unlike
202 flame-retarded plastics more generally and including polyethylene, foamed PS impregnated with
203 HBCD does not require the addition of antimony trioxide (Sb_2O_3) as a synergist to meet various
204 building code specifications (53). On health and environmental grounds, however, HBCD was
205 recently added to Annex A of persistent organic pollutants in the Stockholm Convention that require
206 elimination (54), effectively banning the production and use of the compound in PS foams for
207 buildings (55). The EU has also since introduced a low concentration limit of 0.1% (1000 mg kg^{-1}) by
208 weight for certain brominated compounds, including HBCD, above which items may not be recycled,
209 and a limit of 0.01% (100 mg kg^{-1}) above which products are not permitted for sale (56).

210 Recent focus has been on alternative flame-retardants, resins, or designs for foamed polystyrene,
211 with halogen-free retardants considered best for the environment and human health (57). However,
212 despite the restrictions on HBCD, the flame-retardant continues to be reported in an array of
213 foamed PS consumer products where fire suppression is neither required nor desired, including
214 food-contact articles and general purpose packaging, suggesting a continuing uncontrolled use or
215 recycling of the chemical (58;59). Moreover, it has been forecast that the amount of construction
216 and demolition waste containing HBCD will continue to increase until 2050 (13).

217 The historical use and contemporary recycling of HBCD, together with its persistence in the marine
218 environment, are also reflected by its presence in foamed PS encountered in beach litter and
219 functional maritime constructions throughout the ocean (60;61). For example, in the north Pacific,
220 HBCD was detected in nearly all samples analyzed ($n > 200$) that had been collected after the
221 chemical was listed in the Stockholm Convention, with concentrations ranging from 0.05 to 14,500
222 mg kg^{-1} (61). Some of the highest concentrations, and well above the EU low concentration limit,
223 were reported for aquaculture buoys where flame-retardancy is clearly unnecessary. Significantly,
224 because HBCD is not covalently bonded to the polymer, mobilization into the environment gradually
225 takes place (62), with a lipophilicity ($\log K_{ow} = 5.6$; 63) ensuring that it will readily bind with organic
226 matter and concentrate in organisms.

227 *4.2. Styrene*

228 In theory, the polymerization of styrene results in repeating monomer units that are covalently
229 bonded and difficult to break. In practice, however, this process is incomplete and the styrene
230 monomer and oligomers may contaminate the final foamed PS product.

231 Styrene monomer released from PS is highly reactive towards cell systems and causes widespread
232 metabolic damage, raising concerns about its migration from foamed PS packaging into food (46). In
233 the environment, however, the monomer is rapidly volatilized and readily degraded and is not
234 considered to bioaccumulate (64). On the other hand, the oligomers of styrene appear to present a
235 very low risk to consumers through food packaging but are less mobile and more persistent in the
236 environment (65), with the latter characteristics affording a potential means of assessing
237 contemporary and historical pollution by PS (66). For example, Kwon et al. (67) measured various
238 styrene contaminants (including the trimer, 2,4, 6-triphenyl-1-hexene, and the dimer, 2,4-diphenyl-
239 1-butene) in coastal seawater and beach sand collected from different parts of the world and found
240 that combined concentrations were variable but highest (and up to about $30 \mu\text{g L}^{-1}$ in seawater and
241 30 mg kg^{-1} in sand) along the most populated coastlines. Distributions were attributed to the
242 leaching of the oligomers from weathered, foamed PS on beaches and their subsequent adsorption
243 onto sand, with transfer to seawater taking place via desorption from contaminated sand or more
244 directly through the leaching of the chemicals from floating PS litter. A more recent study suggested
245 that oligomer concentrations in coastal seawater may also be augmented by inputs from
246 contaminated catchment runoff (68).

247 *4.3. Surface modification of foamed PS and acquisition of environmental contaminants*

248 The weathering and chemical and biological fouling of foamed PS, evident in Figure 1e, result in
249 significant modifications to the polymer surface. For example, measurements made by Zhang et al.
250 (30) on virgin and beached EPS revealed an increase in specific surface area (from about 2 to $8 \text{ m}^2 \text{ g}^{-1}$
251 1), micropore area (from < 0.1 to $0.5 \text{ m}^2 \text{ g}^{-1}$), and point of zero charge (from 4.7 to 5.0) on
252 weathering; by comparison, the specific surface area of aged polyethylene is just $0.13 \text{ m}^2 \text{ g}^{-1}$ (69).
253 Not only do these characteristics confer a greater reactivity in the aqueous medium, the high
254 positive buoyancy of foamed PS ensures that it is persistently exposed to a wide array of chemicals
255 in the sea surface microlayer (Figure 2). This is a skin of water of 1 to $1000 \mu\text{m}$ thick enriched in
256 various inorganic salts, hydrophobic or surface-active biogenic compounds, fuels and oils, and
257 various trace contaminants of low solubility or that have been deposited from the atmosphere
258 (70;71). Specifically, concentrations of some pollutants, like chlorinated hydrocarbons and heavy
259 metals, may be up to 500 times higher in the microlayer compared with the underlying bulk water
260 column (72). Hydrophobic chemicals have a propensity to interact with the embrittled and fractured

261 PS surface (47) and, while metal ions are known to readily adsorb onto hydrogenous precipitates on
262 polyethylene (73-75), this has yet to be empirically demonstrated for foamed PS.

263 The acquisition of chemicals from the environment and the more general biological fouling also act
264 to increase the net density of foamed PS. However, and in contrast to unfoamed plastics, this
265 increase is not likely to be sufficient to cause a significant shift in buoyancy or effect sinking unless
266 particles are considerably smaller than the diameter of component PS cells (76).

267

268 **5. Impacts on marine organisms**

269 Foamed PS does not represent a significant risk of entanglement to marine wildlife but can exert
270 impacts through ingestion and interaction.

271 Ingestion of foamed PS may arise directly from the inadvertent consumption of material mistaken
272 for food that is floating in the water column, deposited on beaches, trapped in macroalgae, or acting
273 as a substrate-habitat, and indirectly via the consumption of contaminated prey. Consequently,
274 ingestion has been documented in the stomach contents or fecal matter of a range of marine
275 animals, including crustaceans, fish, birds, turtles, and mammals, and as exemplified in Table 2.
276 Seabirds in particular are commonly observed to ingest foamed PS because floating fragments are
277 similar in size and color to normal prey items like fish, fish eggs, and larvae (90). Birds, those that
278 feed by dipping, fluttering above the surface, surface plunging, surface seizing, and scavenging are
279 most likely to inadvertently ingest PS foam. In addition, distinctive marks on fragments of EPS and
280 XPS retrieved from the shore suggest that some birds, including fulmars and gulls, peck at foamed
281 PS, resulting in the ingestion of small particles (91;92). Pecking may be practiced out of curiosity or
282 through confusion with the brittle and bright white, internal shells of cuttlefish that act as a
283 supplemental source of calcium carbonate.

284 Many of the broad physical impacts resulting from the ingestion of foamed PS are likely to be
285 common to those resulting from the ingestion of other plastics. These include intestinal blockage
286 and injury to the digestive tract, with potential longer-term effects involving reduced body weight
287 and fitness and slower growth. However, given foamed PS's relatively low density, smooth surface,
288 high flexibility, and propensity to fragment, these impacts may be less severe or long-lasting than
289 those effected by harder and sharper plastics like polyethylene. Plastic manufactured or fragmented
290 to dimensions on the order of a few μm or less (nanoplastics) may also be captured by organisms as
291 small as zooplankton and, in many cases, undergo internalization and translocation (93). Regular
292 industrial (unfoamed) PS nanoparticles (density $\sim 1.1 \text{ g cm}^{-3}$) have been frequently studied through

293 in vitro cultures with crustaceans, invertebrates, and fish and have resulted in a range of adverse
294 effects, including delayed growth, repressed immunity, histopathological changes, behavioral
295 changes, and decreased reproduction (94-97). It remains unclear, however, as to whether these
296 effects can be extrapolated to positively-buoyant foamed PS should fragments be weathered down
297 into nanoplastic dimensions.

298 An additional impact resulting from ingestion of foamed PS is the exposure to chemicals associated
299 with the material through manufacturing or acquisition from the environment. Exposure is normally
300 evaluated in vitro by subjecting test material to conditions that mimic the digestive environment and
301 measuring chemical mobilization or bioaccessibility (as an upper bound estimate of bioavailability).
302 Coffin et al. (48) determined the quantities of various organic additives released from sixteen
303 different plastics subjected to solutions representative of the digestive environments of fish and
304 seabirds as well as the estrogen-receptor activities of the resulting extracts using an in vitro cell line.
305 Biological estrogenicity was significantly enhanced by extracts of three plastics (including EPS) in
306 both digestive solutions but the precise additives or residues responsible were not among the
307 chemicals characterized by the authors. Turner and Lau (60) report that neither Br (a proxy for
308 HBCD) nor Zn (indicative of Zn stearate) were detected by ICP in extracts of aged, beached EPS
309 subjected to a simulated avian digest, but that Fe oxide was measurably mobilized (presumably
310 together with any contaminants associated with this phase) from the fouled surface. More sensitive
311 HPLC analysis of HBCD in EPS buoys maintained in dark seawater, however, reveal that the
312 brominated flame-retardant is slowly mobilized from the plastic (62) and, therefore, has the
313 potential to be released under harsher digestive conditions of sea birds and other animals.

314 Interactions refer to a variety of impacts arising from contact of marine organisms with the material
315 as an abiotic substrate and that can also, ultimately, result in plastic ingestion. For instance, certain
316 organisms are able to colonize foamed PS as a rafting substrate, an effect that was originally
317 documented for bacteria growing on EPS beads in the coastal waters of New England (98). More
318 recently, Carson et al. (99) determined concentrations of bacteria up to 12,000 mm⁻² on EPS
319 fragments retrieved from the North Pacific Gyre; by comparison, maximum bacteria concentrations
320 on polyethylene fragments from the same region were < 5000 mm⁻². It has been proposed that the
321 initial colonization of foamed PS is more favorable than on unfoamed plastics because the greater
322 rugosity of the former facilitates adhesion and affords protection (33). Foamed PS, however, displays
323 relatively low species richness because of floating instability; that is, multiple positional changes that
324 incur frequent exposure to air and direct sunlight negatively affect broader colonization (33).
325 Consequently, free-floating, foamed PS likely acts as rafting and dispersing substrate for a limited
326 number of organisms that grow during initial stages of community succession.

327 Jang et al. (100) describe marine mussels, *Mytilus galloprovincialis*, inhabiting the EPS of tethered
328 aquaculture buoys off the coast of South Korea and demonstrated that HBCD is transferred from the
329 substrate to the bivalve with resultant lipid weight concentrations of up to 5.2 mg kg⁻¹. The authors
330 suggest that HBCD is bioaccumulated through the direct ingestion of fragmented EPS particles and
331 via leaching of the chemical and its subsequent adsorption onto food particulates. Aquaculture buoy
332 EPS also hosts a variety of polychaete worms, both at the surface and, via burrowing, within the
333 internal structure (101). Worms both generate and consume debris, with an average of over 100 EPS
334 particles reported in the digestive tracts of burrowing individuals.

335 Filter-feeding sphaeromatid isopods excavate burrows for their habitat and dense colonies are
336 known to cause extensive damage to floating docks constructed of EPS (102). Burrowing may release
337 large fragments of EPS that disperse isopods and are responsible for the generation of significant
338 quantities of microplastics. Laboratory experiments conducted by Davidson (103) suggest that
339 individual bioeroders can create several thousand particles when excavating a burrow, which is
340 equivalent to 100,000 organisms per m³ creating over 400 million particles. Microplastics may then
341 be ingested by a range of organisms, including those that are cultured near to floats for human
342 consumption.

343 Biotic Interactions with foamed PS also take place in reaches of the littoral zone that are never
344 inundated but where debris from both marine sources and beach littering may accumulate. Poeta et
345 al. (25) found that certain dunal plants were able to perforate EPS debris on a sandy beach situated
346 along the Tyrrhenian coast of Italy. Although these observations were attributed to opportunistic
347 events, the authors suggested that the thermal, mechanical, and water absorbing properties of EPS
348 may be generally favorable for this kind of interaction and that the phenomenon might be more
349 widespread on a global scale.

350

351 **6. Emerging solutions to foamed PS waste generation and disposal**

352 The discussions above highlight the problems of foamed PS in the marine environment arising from
353 the quantity and diversity of applications of the material, its low density, ready fragmentation and
354 dispersal in the ocean and littoral environments, the presence of harmful additives, and difficulty in
355 retrieval of waste through, for example, beach cleans. Ultimately, countering these problems
356 requires a reduction in the usage of foamed PS, modification or replacement of the material, or
357 better management and recycling of PS-bearing waste.

358 Alternative materials to or designs of foamed PS require an ability to perform same function (e.g.
359 insulation, fire-retardancy, strength, flotation) and yet be cost-effective, long-lasting, and/or more
360 environmentally sustainable throughout their life cycle. Examples that are becoming more popular
361 or that have been tested but are not widely employed are reported by Lassen et al. (13;104). In the
362 construction sector, alternative materials are mineral and glass wools, phenolic foams, natural
363 fibres, perlite, and wood fibreboards, with a modification of foamed PS that requires less material to
364 achieve equivalent insulation achieved by the addition of graphite. Elsewhere, alternatives include
365 corrugated cardboard for single use products, with polyethylene or polyethylene terephthalate
366 lining where water absorption may be a problem, inflated air packets or molded pulp loose fill for
367 single-use packaging, expanded polypropylene (a more robust foamed plastic) for multi-use
368 packaging, and higher density EPS to enhance abrasion-resistance. In cities, states, and
369 municipalities where restrictions or bans on single-use foamed PS products are in place, many
370 compostable or readily recyclable alternatives have been introduced (19;105;106). Such alternatives
371 also need to be considered for Europe where legislation is being drafted (Directive 2019/904,
372 planned to be effective from July 2021) to ban single-use plastics that include EPS-XPS food and
373 beverage containers (9). (In the UK, recent legislation bans specific single use plastics but thus far no
374 specific mention is made of foamed PS products; 107).

375 In the marine sector, modifications or alternatives to conventional floats and buoys include air-filled
376 plastics, plastic-coated EPS, or EPS contained by netting (108). However, there are additional
377 problems with these constructions, such as increased cost, difficulties in tying to other structures,
378 and enhanced biofouling. Incentive schemes for aquaculture farmers and fishermen to retrieve
379 floating devices constructed of EPS have been trialed in Taiwan but have proven only partly
380 successful, with suggestions that the imposition of a mandatory recovery rate might be more
381 effective (26). Aside from the potential presence of HBCD in marine EPS, however, contamination of
382 recovered material by, for example, salt, sand, oil, and chemical precipitates, precludes it from being
383 recycled.

384 The construction and demolition industries generate significant quantities of foamed PS waste and
385 fugitive particles through a variety of routes, including board cutting, and the storage and transport
386 of material and offcuts. Measures to minimize the escapement of foamed PS from this sector include
387 making employers more aware of environmental damage caused by the material, use of hot wires
388 for cutting, careful separation of demolition waste, covering and securing waste containers, and
389 incentivizing the return of unused material to the manufacturer (13). Demolition waste is of greater
390 concern than contemporary construction waste because of the higher probability of material
391 containing HBCD (109). The presence of this additive may also pose challenges and constraints on

392 how the material can be disposed of and recycled. Rapid screening methods based on portable X-ray
393 fluorescence spectrometry have been developed that detect the presence and solubility of Br in
394 foamed PS (HBCD is solvent-extractable while newer, 'safer' brominated compounds are not) (110).
395 These methods could assist with decisions concerning the fate of demolition waste on site or as a
396 waste disposal input control but to date these do not appear to have been applied on an industrial
397 scale.

398 To summarize, foamed PS has a number of distinctive properties that renders it highly favorable for
399 a wide range of applications across multiple sectors. However, it is this usage and these
400 characteristics that ensure large quantities of foamed PS waste enter the marine environment and
401 present a diversity of pervasive impacts. The chemical and biological risks of foamed PS are further
402 compounded by the widespread occurrence of HBCD in historical and recycled products.
403 Recommendations to reduce these risks and impacts relate to better management of foamed PS
404 throughout its life cycle and replacing the material with more durable and sustainable alternatives.

405

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410 **Supporting Information Available**

411 This information is available free of charge via the Internet at <http://pubs.acs.org>.

412 Table S1 provides information on the physico-chemical and environmental properties of
413 hexabromocyclododecane.

414

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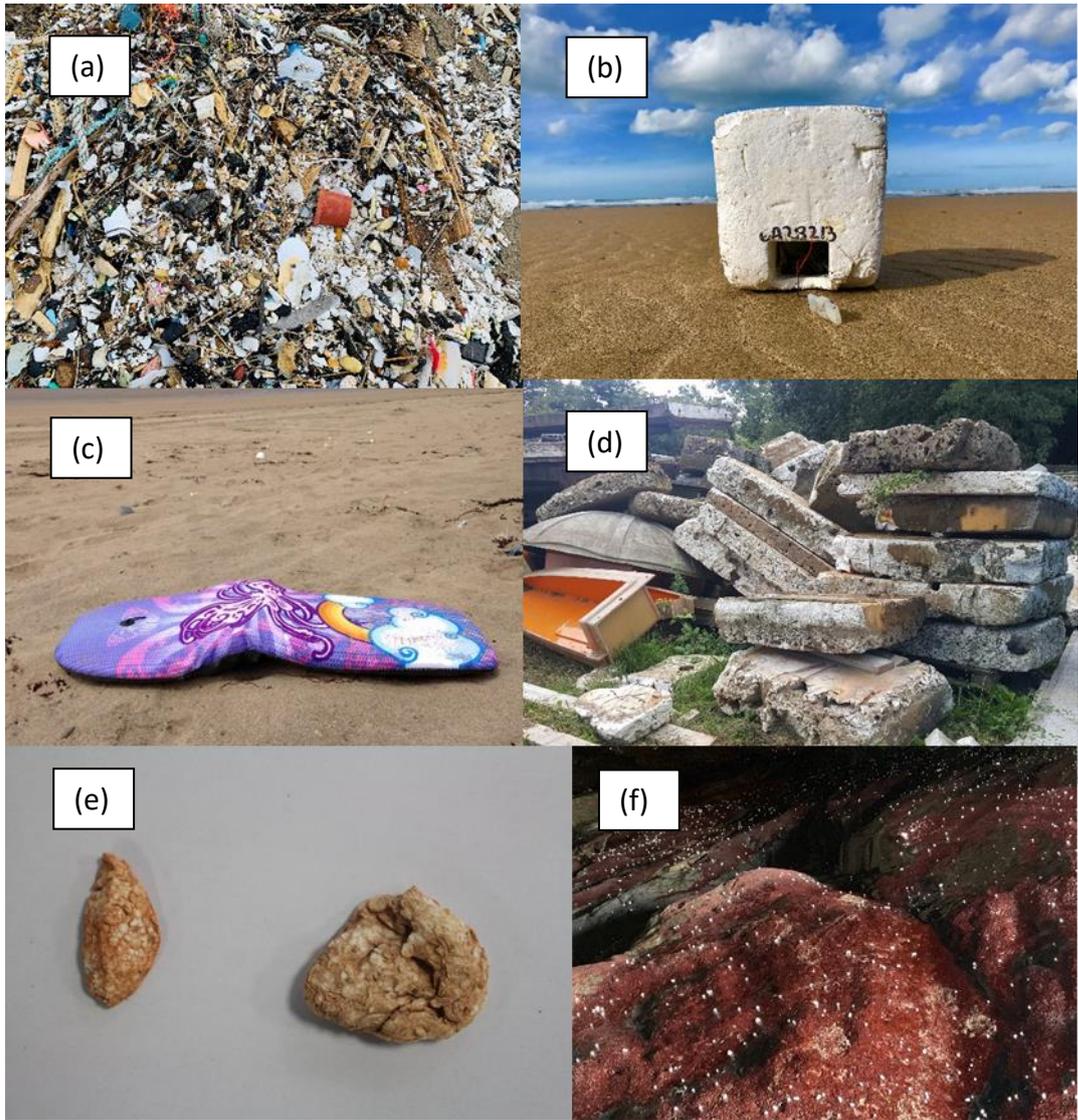
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716 Figure 1: Foamed PS captured around or retrieved from the coast of south-west England. (a) An
717 abundance of EPS and XPS amongst litter along the strandline; (b) EPS remains of a weather balloon;
718 (c) a discarded EPS surfboard; (d) stacked EPS slabs used as boat stands; (e) fouled and rounded
719 fragments of beached EPS and XPS litter; (f) EPS beads scattered at the base of a cliff. Photographs
720 courtesy of Claire Wallerstein and Tracey Williams.

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728 Table 1: The properties of foamed PS of relevance to the discussion. Data are shown for a single,
729 unspecified EPS product or a range of EPS products.

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Property	mean \pm 1 sd or range	source
<u>Physical</u>		
Density	0.01 to 0.19 g cm ⁻³	10
Permeability	0.5 to 3.5	29
Water absorption	0.03 to 9.0%	29
Pore volume	0.02 \pm 0.005 cm ³ g ⁻¹	30
Average pore diameter	39.3 \pm 0.5 nm	30
<u>Mechanical</u>		
Tensile strength, ultimate	0.08 to 0.91 MPa	29
Compressive yield strength	0.069 to 10.9 MPa	29
Tear strength	1.05 to 5.29 kN m ⁻¹	29
<u>Surface</u>		
BET specific surface area	2.03 \pm 0.04 m ² g ⁻¹	30
Point of zero charge	4.7 \pm 0.2	30

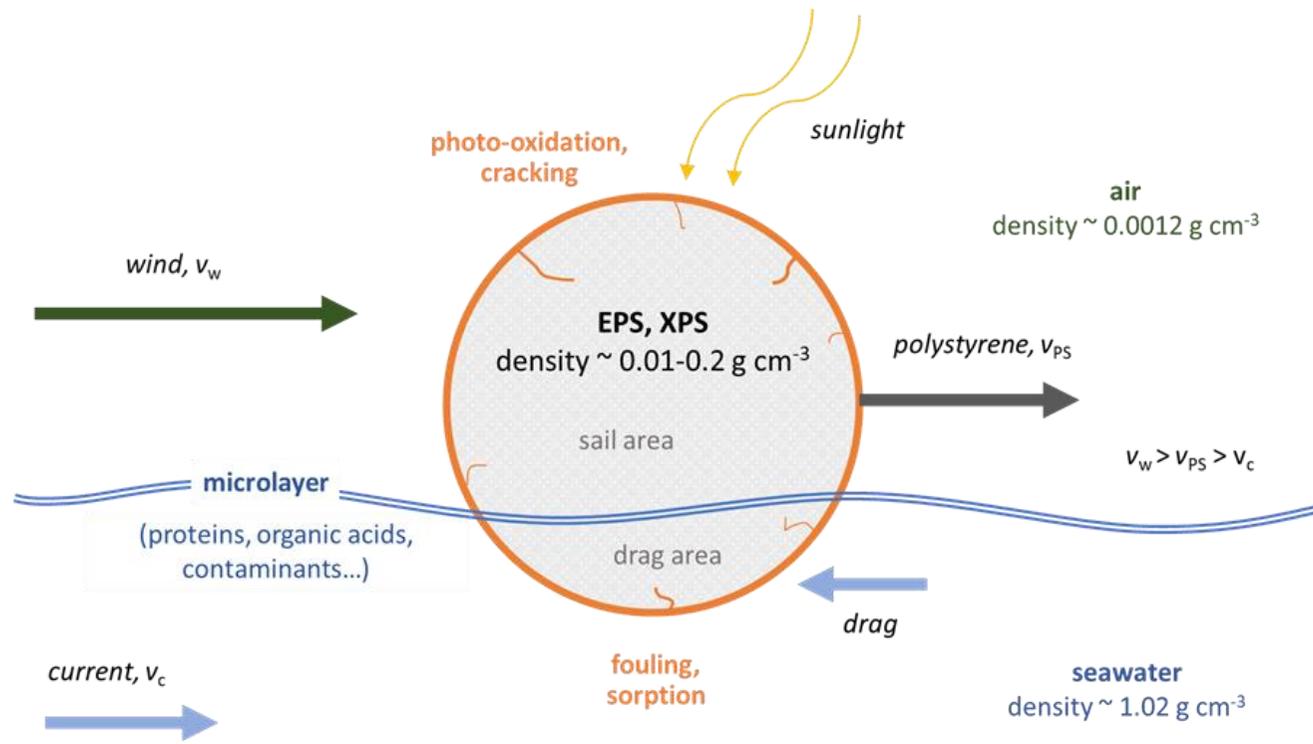


Figure 2: Conceptual representation of the effects and forcing mechanisms acting on a foamed PS sphere in the ocean.

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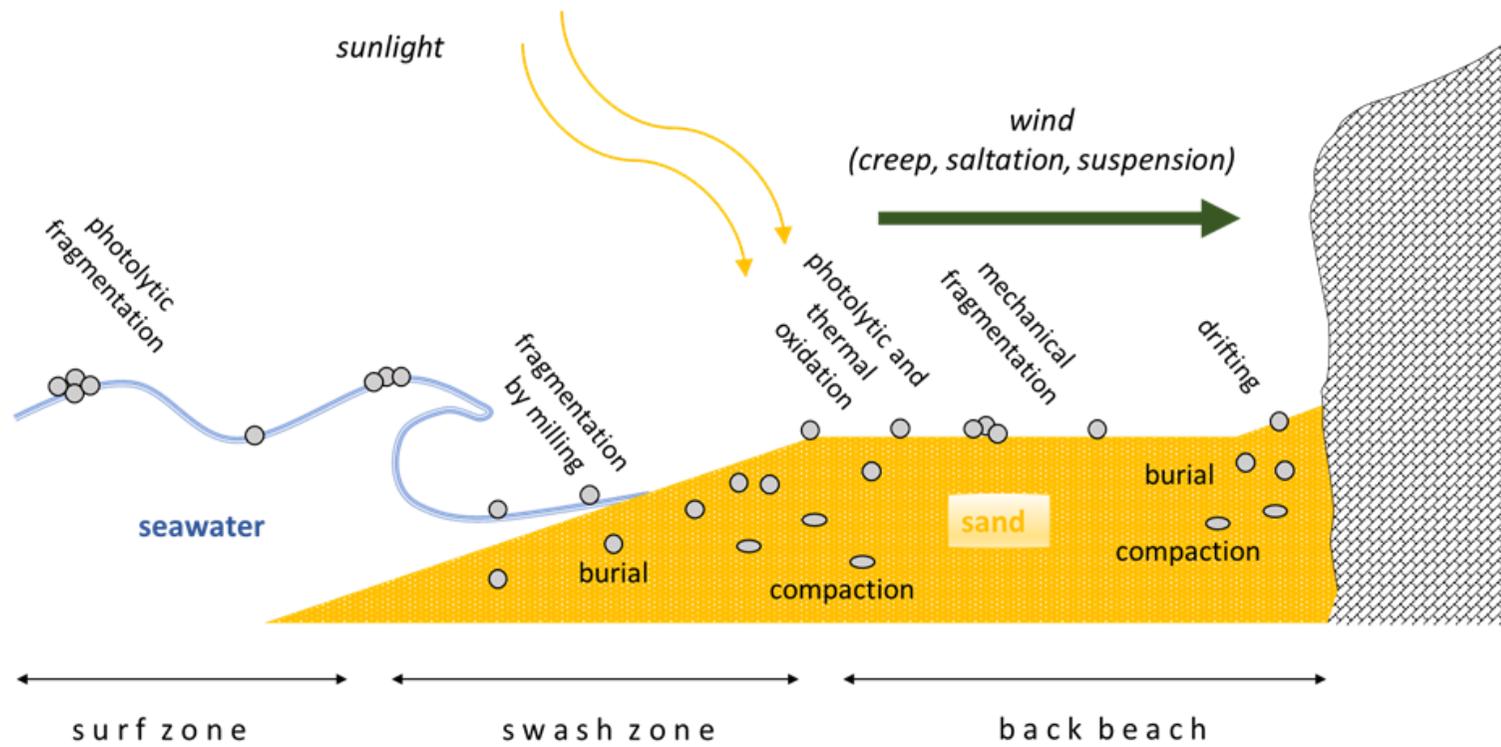


Figure 3: Conceptual representation of the effects and forcing mechanisms acting on foamed PS fragments in the sandy littoral zone.

770 Table 2: Examples of reports of the ingestion of foamed PS by marine wildlife.

Animal	Location	Material description	Reference
Black footed albatross	Central Pacific	foam, including PS	79
Laysan albatross	Central Pacific	foam, including PS	79
Atlantic ghost crab	Southwest Atlantic	XPS	80
Sand hopper	Mediterranean	EPS	81
Blue mussel	English Channel	foamed PS	82
Gooseneck barnacles	North Pacific Subtropical Gyre	foamed PS	83
Kelp gull	Southwest Atlantic	foamed PS	84
Red-footed booby	South China Sea	foamed PS	85
Various albatrosses and petrels	South Atlantic	foamed PS	86
Northern fulmar	Northeast Pacific	Styrofoam	87
Northern fulmar	Northeast Atlantic	expanded PS	88
Green turtle	Southwest Atlantic	XPS	89
Loggerhead turtle	Southwest Atlantic	XPS	89
Narrow-ridged finless porpoise	Yellow Sea-Bohai Sea	foamed PS	90
Elephant seal	Northeast Pacific	Styrofoam	91
Steller sea lion	Northeast Pacific	Styrofoam	91
771 Polychaete worms	Yellow Sea	EPS	103

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