1	Foamed polystyrene in the marine environment: Sources, additives,
2	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, dispersed, and fragmented in the environment. This review focuses on foamed PS in the marine 18 setting, including its sources, transport, degradation, acquisition of contaminants, ingestion by 19 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, hexabromocyclododecane. Because foamed PS is particularly difficult to retrieve as a constituent of 30 31 marine litter, means of reducing its presence and impacts will rely on the elimination of processes that generate foamed waste, modification of current storage and disposal practices, and the 32 33 development of more durable and sustainable alternatives.

34

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: $[CH_2CH(C_6H_5)]_n$; 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 irregular gaps or voids, renders the material susceptible to (limited) water absorption. XPS is formed 65 when PS crystals, additives, and blowing agents are extruded at high temperature to produce a 66 67 frothy liquid that is subsequently shaped in a die as it cools and expands. XPS consists of tightly

packed cells that have no gaps or voids between them. This closed structure inhibits water
absorption and results in a smoother surface and a higher density than EPS. Note that Styrofoam[®] is
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

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

3. Transport and physical behavior in the marine environment

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

110

111 *3.1. In the ocean*

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

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 wind forces (31). Specifically, and neglecting any phenomena incurred by viscous forces, wind 118 119 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 ~ 1.01 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
- 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
- times and 25% higher than v_c . In other words, and under these environmental conditions, foamed PS

whose density is not significantly modified by fouling (see below) is predicted to travel three timesfaster 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 generated by a metal-halide lamp was sufficient to break EPS beads (~ 20 mm³) into microfragments, 141 142 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*

Ultimately, a significant fraction of both oceanic and land-derived foamed PS will end up in the
littoral zone, including mangroves, beaches, and rocky shores (19;20;24). The effects and forcing
mechanisms acting upon this type of litter on a sandy shoreline are conceptualized in Figure 3 as an
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 μ m) to be detected (37;40).

Mechanical fragmentation of foamed PS also takes place in the swash zone where litter already
 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

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

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

181 Residues in foamed PS include Fe₂O₃, used as a catalyst in the production of styrene (43), and Zn stearate, often used to ensure uniform cell nucleation in the production of EPS (44). Additives are 182 183 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*

Flame-retardants are added to foamed PS destined for the construction industry but are alsoencountered 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).

Recent focus has been on alternative flame-retardants, resins, or designs for foamed polystyrene, with halogen-free retardants considered best for the environment and human health (57). However, despite the restrictions on HBCD, the flame-retardant continues to be reported in an array of foamed PS consumer products where fire suppression is neither required nor desired, including food-contact articles and general purpose packaging, suggesting a continuing uncontrolled use or recycling of the chemical (58;59). Moreover, it has been forecast that the amount of construction 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 environment, are also reflected by its presence in foamed PS encountered in beach litter and 218 219 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 unneccessary. 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

In theory, the polymerization of styrene results in repeating monomer units that are covalently
bonded and difficult to break. In practice, however, this process is incomplete and the styrene
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 μ g L⁻¹ in seawater and 30 mg kg⁻¹ in sand) along the most populated coastlines. Distributions were attributed to the 241 242 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

The weathering and chemical and biological fouling of foamed PS, evident in Figure 1e, result in 248 249 significant modifications to the polymer surface. For example, measurements made by Zhang et al. (30) on virgin and beached EPS revealed an increase in specific surface area (from about 2 to 8 m² g⁻ 250 ¹), micropore area (from < 0.1 to 0.5 m² g⁻¹), and point of zero charge (from 4.7 to 5.0) on 251 252 weathering; by comparison, the specific surface area of aged polyethylene is just 0.13 m² 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 μ 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 PS surface (47) and, while metal ions are known to readily adsorb onto hydrogenous precipitates on
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

to increase the net density of foamed PS. However, and in contrast to unfoamed plastics, this

- 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**

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

Ingestion of foamed PS may arise directly from the inadvertent consumption of material mistaken 271 272 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

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 and fitness and slower growth. However, given foamed PS's relatively low density, smooth surface, 287 288 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 μ m 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 ~ 1.1 g cm⁻³) have been frequently studied through

in vitro cultures with crustaceans, invertebrates, and fish and have resulted in a range of adverse
effects, including delayed growth, repressed immunity, histopathological changes, behavioral
changes, and decreased reproduction (94-97). It remains unclear, however, as to whether these
effects can be extrapolated to positively-buoyant foamed PS should fragments be weathered down
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 potential to be released under harsher digestive conditions of sea birds and other animals. 313

314 Interactions refer to a variety of impacts arising from contact of marine organisms with the material as an abiotic substrate and that can also, ultimately, result in plastic ingestion. For instance, certain 315 316 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 on polyethylene fragments from the same region were < 5000 mm⁻². It has been proposed that the 320 321 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 known to cause extensive damage to floating docks constructed of EPS (102). Burrowing may release 336 337 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.
- Biotic Interactions with foamed PS also take place in reaches of the littoral zone that are never inundated but where debris from both marine sources and beach littering may accumulate. Poeta et al. (25) found that certain dunal plants were able to perforate EPS debris on a sandy beach situated along the Tyrrhenian coast of Italy. Although these observations were attributed to opportunistic events, the authors suggested that the thermal, mechanical, and water absorbing properties of EPS may be generally favorable for this kind of interaction and that the phenomenon might be more widespread on a global scale.
- 350

6. Emerging solutions to foamed PS waste generation and disposal

The discussions above highlight the problems of foamed PS in the marine environment arising from the quantity and diversity of applications of the material, its low density, ready fragmentation and dispersal in the ocean and littoral environments, the presence of harmful additives, and difficulty in retrieval of waste through, for example, beach cleans. Ultimately, countering these problems requires a reduction in the usage of foamed PS, modification or replacement of the material, or 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
- 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
- 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 <u>http://pubs.acs.org</u>.
- 412 Table S1 provides information on the physico-chemical and environmental properties of413 hexabromocyclododecane.
- 414

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

728 Table 1: The properties of foamed PS of relevance to the discussion. Data are shown for a single,

unspecified EPS product or a range of EPS products.

Property	mean <u>+</u> 1 sd or range	source
Physical		
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 <u>+</u> 0.005 cm ³ g ⁻¹	30
Average pore diameter	39.3 <u>+</u> 0.5 nm	30
Mechanical		
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
Surface		
BET specific surface area	2.03 <u>+</u> 0.04 m ² g ⁻¹	30
Point of zero charge	4.7 <u>+</u> 0.2	30





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
Polychaete worms	Yellow Sea	EPS	103