

1 **Polystyrene plastic: a source and sink for polycyclic aromatic hydrocarbons in the marine**
2 **environment**

3 Chelsea M. Rochman^{1§}, Carlos Manzano^{2§}, Brian T. Hentschel¹, Staci L. Massey Simonich^{2,3},
4 Eunha Hoh^{4*}

5
6 ¹Department of Biology and Coastal and Marine Institute, San Diego State University, San
7 Diego, CA

8 ²Department of Chemistry, Oregon State University, Corvallis, OR

9 ³Department of Environmental and Molecular Toxicology, Oregon State University,
10 Corvallis, OR

11 ⁴Graduate School of Public Health, San Diego State University, San Diego, CA

12
13 *Corresponding Author (ehoh@mail.sdsu.edu)

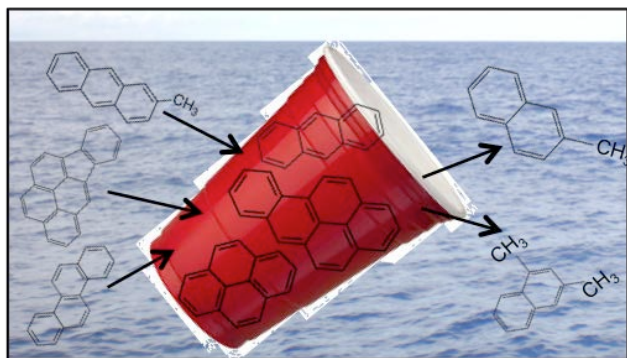
14 §Manzano and Rochman are equal contributors to the manuscript.

15 The current address for Chelsea Rochman is the Aquatic Health Program, University of
16 California, Davis, CA and for Carlos Manzano is the Canada Centre for Inland Waters,
17 Burlington, Ontario, Canada

18 **Abstract**

19 Polycyclic aromatic hydrocarbons (PAHs) on virgin polystyrene (PS) and PS marine
20 debris led us to examine PS as a source and sink for PAHs in the marine environment. At two
21 locations in San Diego Bay, we measured sorption of PAHs to PS pellets, sampling at 0, 1, 3, 6,
22 9 and 12 months. We detected 25 PAHs using a new analytical method with comprehensive two-
23 dimensional gas chromatography coupled to time-of-flight mass spectrometry. Several congeners

24 were detected on samples before deployment. After deployment, some concentrations decreased
25 (1,3-dimethylnaphthalene and 2,6-methylnaphthalene) while most increased (2-methylantracene
26 and all parent PAHs (PPAHs) except fluorene and fluoranthene), suggesting PS debris is a
27 source and sink for PAHs. When comparing sorbed concentrations of PPAHs on PS to the five
28 most common polymers (polyethylene terephthalate (PET), high-density polyethylene (HDPE),
29 polyvinyl chloride (PVC), low-density polyethylene (LDPE), and polypropylene (PP)), PS
30 sorbed greater concentrations than PP, PET and PVC, similar to HDPE and LDPE. Most
31 strikingly, at 0 months, PPAHs on PS ranged from 8-200 times greater than on PET, HDPE,
32 PVC, LDPE, and PP. The combination of greater PAHs in virgin pellets and large sorption
33 suggests that PS may pose a greater risk of exposure to PAHs upon ingestion.



34
35 **Introduction**

36 Plastics debris is ubiquitous across several habitats in the marine environment from beaches¹
37 to the open ocean² extending to the depths of the sea³. Priority pollutants (e.g. persistent organic
38 pollutants) are consistently found sorbed to this debris from seawater⁴ and are associated with
39 plastics as ingredients and/or byproducts of manufacturing⁵. Thus, when determining the risk of
40 plastic marine debris to an organism, it is important to consider the chemical ingredients and the
41 sorbed priority pollutants^{6,7}. For example, we found similarly large levels of polycyclic aromatic

42 hydrocarbons (PAHs) on polystyrene (PS) foam packaging materials as we did on PS foam
43 debris recovered from beaches⁸, suggesting that PAHs are associated with plastic debris via
44 absorption and manufacturing. Here, we examine this further and use PS pellets to measure PS
45 debris as both a source and sink for PAHs in the marine environment.

46 PAHs are ubiquitous contaminants generated during the incomplete combustion of organic
47 material^{9,10} and are considered a priority due to their persistence, bioaccumulation and
48 toxicity^{11,12}. In water, PAHs tend to associate with particles rather than dissolve due to their
49 hydrophobic nature¹³, and thus plastics are used as passive samplers to measure PAHs in
50 seawater¹⁴. The large sorption of PAHs to polyethylene¹⁴ and polyurethane foam¹⁵ is well
51 known. Thus, it is expected that plastic debris will act as a sink for PAHs in aquatic habitats and
52 it is no surprise that plastic debris recovered globally contains measurable PAHs⁴.

53 To understand sorption of PAHs to different types of plastic debris, we conducted the
54 first long-term controlled field experiment designed to measure sorption of several priority
55 pollutants, including PAHs, in the marine environment to the six most commonly mass-produced
56 polymers (polyethylene terephthalate (PET), high-density polyethylene (HDPE), polyvinyl
57 chloride (PVC), low-density polyethylene (LDPE), polypropylene (PP) and PS).^{6,16} Virgin pre-
58 production pellets of each polymer were deployed at five locations throughout San Diego Bay,
59 CA for five time periods up to one year and showed that HDPE, LDPE, PP and PVC sorbed
60 significantly different concentrations of PAHs.⁶ We were unable to determine sorption to PS
61 because chemical analyses were unsuccessful using a conventional one-dimensional GC/MS
62 method due to the complexity of the sample matrix. Here, we applied a recently developed
63 method based on comprehensive two-dimensional gas chromatography (GC×GC/ToF-MS)¹⁷ to

64 successfully analyze parent-PAHs (PPAHs), alkyl-PAHs (MPAHs), nitro-PAHs (NPAHs), oxy-
65 PAHs (OPAHs) and thio-PAHs (SPAHS) within one single chromatographic run.

66 Here, we analyzed multiple classes of PAHs on PS pellets deployed in San Diego Bay for
67 up to one year to test the hypotheses that 1) PAHs are associated with virgin PS, 2) PAHs will
68 sorb to PS in the marine environment from several sources and 3) concentrations will differ from
69 other plastic types. This work provides insight into potential hazards associated with PS marine
70 debris. PS is a common marine debris item¹⁸ and has been found in the gut contents of fish.¹⁹ In
71 the absence of PAHs, PS poses a hazard to marine organisms due to its hazardous styrene
72 monomer, both carcinogenic and disruptive to the endocrine system.²⁰ Here, we show that
73 several PAHs are associated with PS before deployment and when littered in the marine
74 environment sorb greater concentrations of these hazardous chemicals. Thus, individual hazards
75 associated with both PS and PAHs make PS marine debris a potential multiple stressor in marine
76 habitats when available for ingestion by marine life.

77

78 **Experimental section**

79 *Experimental Design*

80 PS virgin pre-production plastic pellets (3 mm long, 2 mm diameter) were deployed from
81 floating docks in San Diego Bay.⁶ Here, we focus on two locations (Figure S1): San Diego
82 Harbor Excursions in the central bay and Shelter Island near the mouth of the bay. Details
83 regarding experimental design can be found in Rochman et al.⁶ Briefly, at each location, two
84 replicate samples were deployed for collection at the end of five time periods: 1, 3, 6, 9, and 12
85 months (20 total samples). Each replicate consisted of 5 g of pellets in individual Nitex mesh

86 (1.3 mm) bags within a nylon mesh (10 mm) bag. Replicate samples were deployed by hanging
87 each nylon bag on one of two identical PVC frames suspended from each dock (approximately 2
88 meters from each other, and at a depth approximately 0.5 m below the surface). At the end of
89 their randomly assigned deployment time, samples were collected and stored at -20°C until
90 analysis. We also analyzed three replicate samples of virgin pellets never deployed in the bay
91 (i.e., 0-month samples). Methods for preparing samples for chemical analyses were established
92 previously in our laboratory⁸ and are described by Rochman et al.⁶. For more information
93 regarding chemical standards and solvent materials, sample prep, chemical analyses and QA/QC
94 refer to Supporting Information.

95 *GC×GC/ToF-MS Analysis for PAHs*

96 A GC×GC/ToF-MS Pegasus 4D (LECO, St. Joseph, MI, USA) equipped with an Agilent
97 6890 GC with a secondary oven, a split/splitless injector, and a non-moving quad-jet dual stage
98 modulator was used. Two GC columns, LC-50 (10 m × 0.15 mm × 0.10 μm) in the first
99 dimension and NSP-35 (1.2 m × 0.10 mm × 0.10 μm) in the second dimension (from J&K
100 Scientific; Edwardsville, Nova Scotia, Canada), were connected using an Agilent CPM union
101 (part no. 188-5361) for 0.1-0.25 mm I.D. columns. The data processing was performed using
102 ChromaTOF version 4.33. The optimization parameters are described in previous studies^{17,24} and
103 optimized conditions in Table S1. Five-point calibration curves with range 5-1000 pg/uL were
104 used, using the same approach that has been described previously²⁴.

105 *Statistical Methods*

106 We quantified temporal patterns by fitting a first-order approach to equilibrium model²⁵ when
107 concentrations appeared to be increasing and an exponential decay model when concentrations
108 appeared to be decreasing²⁶. SigmaPlot 10 (SYSTAT Software, Chicago, IL) was used to fit the

109 exponential rise to maximum, $C_t=C_{eq}(1-e^{-kt})$, and the exponential decay, $C_t=(C_0-C_{eq})e^{-kt} + C_{eq}$,
110 equations where C_t is the concentration at time t , C_{eq} is the predicted equilibrium concentration,
111 C_0 is the initial concentration and k is the rate constant. We examined spatial patterns using
112 principle components analysis (PCA) run with IBM SPSS version 19 and potential sources using
113 molecular ratios of several PAHs at each location. This method involves comparing
114 concentration ratios of frequently found PAHs to identify possible sources²⁷ and should be used
115 with caution because molecular ratios can easily be altered by different factors such as reactivity
116 of PAHs and degradation.²⁷⁻²⁹ The combination of five molecular ratios containing fluorene
117 (FLO), pyrene (PYR), anthracene (ANT), phenanthrene (PHE), benzo[a]pyrene (BaP), chrysene
118 (CHR), benz[a]anthracene (BaA), Triphenylene (TRI), benzo[b]fluoranthene (BbF) and
119 benzo[k]fluoranthene (BkF) were used to generate bi-variate plots (Figure 5).³⁰⁻³³ Two-sample
120 student t -tests run in SigmaPlot 10 (SYSTAT Software, Chicago, IL) determined if
121 concentrations of PAHs and molecular ratios were statistically different between locations.
122 Concentrations of total sorbed PPAHs were log-transformed to achieve normality. We tested for
123 differences among plastic types and locations in San Diego Bay by performing a 2-factor
124 ANOVA on data from each sampling period individually with SYSTAT 12 (SYSTAT Software,
125 Chicago, IL). Data for PPAHs sorbed to HDPE, LDPE, PP, PET and PVC deployed
126 simultaneously with PS was included in this analysis.⁶ Homogeneity of variance was verified by
127 a Levene's test. Post-hoc Tukey's tests were used to distinguish significantly different treatment
128 means.

129

130 **Results and Discussion**

131 *PAH analysis achieved by the GC×GC/ToF-MS method*

132 The one-dimensional GC-MS method⁶ previously used for analysis of PAHs in other
133 plastic types was unsuccessful for the PS samples. The column was sacrificed due to column
134 overload and strong matrix interferences that can be seen as very large peaks eluting at the
135 beginning of the run in selected ion monitoring (SIM) chromatogram (Figure 1). The inner boxes
136 in Figure 1 show PAHs co-eluting with interfering components represented by large peaks that
137 do not correspond to any PAH or internal standard.

138 Figure 2 shows the total ion chromatogram (TIC) for the analysis of a PS sample using
139 the GC×GC/ToF-MS method developed for simultaneous analysis of multiple groups of
140 PAHs,^{17,24} where the sample matrix (represented by dashed lines) elutes in regions that do not
141 interfere with most of the PAHs (represented by a dotted line). This two-dimensional method
142 was successful to analyze a total of 85 PAHs for identification and quantitation in PS samples,
143 including 18 PPAHs, 9 MPAHs, 15 CIPAHs, 6 BrPAHs, 17 OPAHs and 2 SPAHs (See Table S2
144 for a complete list of targeted PAHs).

145 *PAHs in PS*

146 A total of 25 PAHs (15 PPAHs, 7 MPAHs, 2 OPAHs and 1 SPAH) were detected in the
147 PS samples. Table 1 shows the concentrations of all PAHs detected (in ng/g) at each sampling
148 period (0, 1, 3, 6, 9, and 12 months) from each location. Congeners from each group were found
149 in virgin PS pellets before deployment. Of the PPAHs, acenaphthene, acenaphthylene,
150 anthracene, fluoranthene, fluorene, phenanthrene and pyrene were found in virgin PS pellets.
151 These seven PAHs have the lowest molecular weight (MW) of the PPAHs targeted and have a
152 log K_{ow} (octanol-water partitioning coefficient) less than or equal to five. Low molecular weight
153 PAHs are characterized to come from direct petrogenic sources³⁴, including the raw material
154 petroleum. Of the MPAHs, 1,3-dimethylnaphthalene, 2,6-dimethylnaphthalene, 1-

155 methylphenanthrene and 2-methylphenanthrene, were found in virgin PS pellets. MPAHs are an
156 associated byproduct of petroleum emissions.³⁵ Both OPAHs, 9-fluorenone and 1,4-
157 naphthoquinone, were measured in virgin PS pellets and can be formed from the incomplete
158 combustion of organic material³⁶, including petroleum. Dibenzothiophene, also found in virgin
159 PS pellets, occurs naturally in the production of oil.³⁷ Because PAHs are associated with
160 petroleum, the raw material of plastics, this is expected.

161 The detection of PAHs in virgin PS pellets adds additional information to previous work
162 showing that PS virgin pellets have up to two orders of magnitude greater concentrations of
163 PPAHs than other polymers.⁸ When comparing PAHs in virgin PS pellets quantified here to
164 those measured in other types of plastic by Rochman et al. (2013)⁶ we find that PPAHs in virgin
165 pellets range from nd-2 ng/g on PVC, nd -1 ng/g in PET, 2-6 ng/g in PP, 3-6 ng/g on HDPE and
166 nd-13 ng/g in LDPE; however, in virgin PS pellets PPAHs range from 79-97 ng/g (n=3),
167 approximately 8 to 200 times greater than other polymers. This large difference in PPAHs in PS
168 virgin pellets strengthens our hypothesis that PAHs are associated with the manufacturing
169 process, likely related to the aromaticity of the styrene monomer.^{8,38}

170 PAH formation may arise from multiple stages in the life cycle of PS. To manufacture
171 polystyrene, ethylene and benzene are produced from crude oil under applied heat.³⁹ The styrene
172 monomer is contrived by reacting benzene with ethylene to make ethyl benzene which is
173 dehydrogenated to styrene at 550-680°C.³⁹ Both benzene and styrene are precursors of PAH
174 formation.⁴⁰ Once polymerized, polystyrene is more capable of depolymerizing into its
175 individual monomers than other polymers²⁰, and because polymerization reactions are rarely
176 complete, the residual monomer styrene is likely to be found in the polymeric product.²⁰ Thus,
177 the monomer styrene is likely available for PAH formation during and post-manufacturing. Once

178 PS pre-production pellets are produced, manufacturers apply heat again to process and shape end
179 products from PS pellets³⁹, likely resulting in emission of more PAHs. Lastly, combustion of PS
180 waste products results in greater PAH emissions than other polymers.⁴¹

181 Temporal patterns among individual congeners of PAHs were examined to better
182 understand PS as a source and sink for PAHs in the marine environment. We quantified temporal
183 patterns by fitting a first-order approach to equilibrium model²⁵ when concentrations of PAHs
184 increased over time and an exponential decay model when concentrations decreased²⁶. Fitting
185 these equation assumes a relatively constant background concentration of PAHs. Although this
186 assumption likely does not hold during a field deployment, the equations fit our data relatively
187 well over the long time scales of our experiment despite temporal variability. Where
188 concentrations of PAHs were relatively constant during deployment, neither model could be fit.
189 Because sorption is related to the hydrophobicity of each specific congener, we quantified
190 temporal patterns for individual PAHs sorbed to PS at each location (Figure 3, S2, S3). To
191 compare sorption trends of PS analyzed here to the HDPE, LDPE, PP, PET and PVC analyzed
192 previously⁶, we also quantified temporal patterns for sorption of total priority PPAHs at Harbor
193 Excursion where concentrations are greatest (Figure S4).

194 We observed PS behaving as a source or a sink for several PAH congeners in San Diego
195 Bay. Yet, for some congeners, we did not observe PS behaving as either. Concentrations of 1-
196 methylphenanthrene, 2-methylphenanthrene, 9-fluorenone, 1,4-naphthoquinone, dibenzothiophene,
197 fluorene and fluoranthene remained relatively constant over time (Figure 3, S2, S3).
198 Concentrations of 1,3-dimethylnaphthalene and 2,6-methylnaphthalene decreased upon
199 deployment (Figure 3, S2), suggesting that PS may be a source of these PAHs to the marine
200 environment. While, these low molecular weight 2-ring PAHs do have a greater solubility in

201 water than other PAH congeners, another explanation may be that these compounds underwent
202 degradation due to exposure to sunlight and/or marine microorganisms. We observed PS
203 behaving as a sink for several PAHs measured in this study, including 1-methylpyrene, 2-
204 methylanthracene and all measured PPAHs except fluorene and fluoranthene (Figure 3, S2, S3).
205 At Harbor Excursion, where concentrations of PAHs were greatest, these PAHs fit the first-order
206 kinetics model well; whereas, at Shelter Island, sorption trends for 1-methylpyrene (non-detect),
207 acenaphthylene, acenaphthene and pyrene could not be fit to the equation.

208 For PAHs sorbed to PS from ambient seawater, we expected individual congeners to
209 behave differently, as chemicals with less hydrophobicity and a lighter MW are expected to
210 reach saturation faster than those with greater hydrophobicity and a heavier MW.⁴² While we
211 observed this for PPAHs sorbing to HDPE, LDPE and PP at Harbor Excursion⁶, similar to PET
212 and PVC⁶ we did not see obvious differences in sorption patterns among individual congeners for
213 PS at either location (Figure S3). Differences in sorption patterns among congeners may not be
214 expected for the glassy polymers, PET, PVC and PS, where diffusion into the polymer is not
215 expected.⁴³ Thus, these polymers may exhibit a relatively rapid adsorption onto the surface that
216 is not followed by a slower diffusion into the polymeric matrix as is expected for polyethylene.⁴²

217 While sorbed concentrations of total PPAHs on PS are similar to HDPE and LDPE, the
218 time to reach predicted equilibrium happens much faster (Figure S4). After the 1-month
219 sampling period, concentrations of total PPAHs sorbed to PS changed little over time at both
220 locations (Table 1). Temporal patterns for PS at Harbor Excursion are similar to what is observed
221 for PET and PVC.⁶ In contrast, at this location HDPE, LDPE and PP reached their predicted
222 equilibriums by 6 months.⁶ Thus, the relatively large concentrations of PPAHs sorbing to PS
223 occurs relatively quickly after deployment into the marine environment (Figure S4).

224 Management of PS may hold a greater priority than debris composed of HDPE, LDPE, PP, PET
225 or PVC because our data suggests that PS acquires relatively large concentrations of hazardous
226 chemicals after a short period of time at sea.

227 *Site difference for PAHs*

228 Total PAH concentrations were greater at Harbor Excursion compared to Shelter Island
229 by a factor of approximately two (Table 1). Concentrations of 21 of the 25 individual PAHs
230 quantified were significantly greater ($p < 0.05$) at Harbor Excursion than Shelter Island, whereas
231 2,6-dimethylnaphthalene, phenanthrene, 9-fluorenone, and 1,4-naphthaquinone were not
232 statistically different ($p > 0.05$) between locations. Concentrations of these four PAHs, with the
233 exception of phenanthrene, decreased or did not change over time. Significant differences among
234 the remaining PAHs are probably related to different sources of contamination between
235 locations.

236 Table S3a and S3b show the PAH compositional difference (%) of the two locations
237 compared to the virgin blanks (0-month exposure). The PAH composition of each sample was
238 compared using principle component analysis (PCA) due to the many variables (25 PAHs). The
239 analysis shows that the top three components (P1-P3) explain 97% of the variance, with P1 =
240 79%, P2 = 11%, and P3 = 7.5%. The PAH composition of the virgin PS pellets was clearly
241 different from the deployed PS pellets (Figure 4). Among the deployed PS pellets, the PAH
242 composition was slightly different between the two sites except one sample from Harbor
243 Excursion (sampled at 6 months; Figure 4). Differences in PAH compositions suggest different
244 sources of PAHs.

245 To further examine sources of PAHs at each location, we used molecular ratios. The
246 FLO/(FLO+PYR) ratio was significantly different between sites ($p < 0.001$), averaging 0.421

247 (± 0.106) at Harbor Excursion and $0.633 (\pm 0.067)$ at Shelter Island, suggesting a gasoline origin
248 for PAHs at Harbor Excursion and a diesel origin for PAHs at Shelter Island (Figure 5A). The
249 ANT/(ANT+PHE) ratio was also significantly different between sites ($p < 0.001$), averaging
250 $0.307 (\pm 0.073)$ for Harbor Excursion and $0.128 (\pm 0.025)$ for Shelter Island, suggesting a
251 pyrogenic origin for PAHs at Harbor Excursion and a more petrogenic origin at Shelter Island
252 (Figure 5A, 5B and 5D) which is reinforced by the ratio BaA/(BaA+CHR+TRI) that was also
253 significantly different between locations ($p < 0.001$), averaging $0.397 (\pm 0.023)$ for Harbor
254 Excursion and $0.346 (\pm 0.015)$ for Shelter Island (Figure 5C). The two ratios BbF/BkF and
255 BaP/(BaP+CHR) were not significantly different between locations. These results suggest that
256 PAHs at Shelter Island and Harbor Excursion come from different sources, with Shelter Island
257 showing ratios closer to those found in petroleum and Harbor Excursion closer to those found in
258 the generation of pyrogenic PAHs. The suggestion that sources of PAHs to Harbor Excursion are
259 more pyrogenic in origin is further confirmed by our data. For example, dibenzothiophene and 1-
260 methylpyrene, with greater concentration at Harbor Excursion, are indicators of fossil fuels such
261 as gasoline or diesel exhaust.^{44,45} In addition, MPAHs are indicative of direct petroleum
262 emissions³⁵, and we found greater concentrations of 1-methylpyrene and 2-methylanthracene at
263 Harbor Excursion relative to Shelter Island likely due to the greater shipping activity at Harbor
264 Excursion.

265 *PPAH concentrations in PS compared to other mass-produced polymers*

266 Upon comparing sorbed concentrations of PPAHs in PS to HDPE, LDPE, PP, PET and
267 PVC previously reported, we found similar patterns confirming our past results showing that
268 HDPE and LDPE sorb significantly greater PAHs than PP, PET and PVC and that PP sorbs an
269 intermediate concentration.⁶ The inclusion of PS in a 2-factor ANOVA for each sampling period

270 reveals a consistently significant interaction ($p < 0.05$) between location and plastic type. Still,
271 over space and time, HDPE, LDPE and PS consistently sorb the greatest concentration of
272 PPAHs. At Shelter Island PS sorbs the greatest concentration of PPAHs overall, but at Harbor
273 Excursions differences among HDPE, LDPE and PS are less conspicuous (Figure 6).

274 Sorption of PPAHs to PS is relatively large (up to 925.6 ng/g; Table 1) when comparing
275 among the other five most commonly produced polymers (HDPE, LDPE, PP, PET and PVC).¹⁶
276 This result may be unexpected based upon the physical nature of PS. Non-expanded PS pellets
277 are in a glassy state, similar to PET and PVC, suggesting a lower diffusivity than polyethylene, a
278 rubbery polymer.⁴³ Moreover, the polymeric backbone of polystyrene has a benzene molecule
279 where polyethylene has a hydrogen, restricting segmental mobility within the polystyrene
280 chains.⁴³ In contrast, the presence of benzene increases the distance between adjacent polymeric
281 chains, which can make it easier for a chemical to diffuse into the polymer.⁴³ Therefore, although
282 polyethylene has greater segmental mobility than PS, PS has a greater distance between
283 polymeric chains, and may explain why we observed similar concentrations of PAHs in PS as we
284 did polyethylene. Moreover, polystyrene foam is one of the most common materials used for
285 solid phase extraction (SPE)⁴⁶ due to the contribution of π - π and strong hydrophobic interactions
286 to retention⁴⁷, suggesting that environmental sorption to PS may be large, specifically for
287 aromatic compounds such as PAHs. Because several factors influence the uptake of a compound
288 to a polymer, including physical and chemical properties of the chemical sorbent, measuring
289 sorption of other groups of chemicals to PS is recommended.

290 *Hazards of PS littered in habitats*

291 The mixture of several PAHs, including oxy-, methyl- and thio-PAHs, in virgin PS
292 pellets may pose a risk to organisms immediately upon being discarded into marine habitats due

293 to the mixture of PAHs in the absence of environmental sorption and its carcinogenic and
294 potentially endocrine disrupting styrene monomer.²⁰ Thus, it is important to consider risks to
295 terrestrial and aquatic wildlife from PS litter. In addition, the combination of greater PAHs on
296 virgin PS pellets and relatively large concentrations of sorbed PAHs from ambient seawater,
297 suggests that PS may pose a greater risk of exposure to PAHs when it is ingested by marine
298 animals than the other most commonly produced plastic-types (HDPE, LDPE, PP, PET and
299 PVC). Future work should measure sorption of other priority pollutants (e.g. PCBs, metals) to
300 PS. The mixture of the PS monomer itself, chemicals from the manufacturing process and those
301 sorbed from the environment may act as a multiple stressor to several species^{19,48} that ingest PS
302 debris. Testing this theory requires additional research that measures adverse health effects from
303 dietary exposure of virgin PS and PS deployed in the marine environment to organisms.

References

- 304 1. Browne, M. A.; Crump, P.; Niven, S. J.; Teuten, E. L.; Tonkin, A.; Galloway, T.; Thompson,
305 R. C. Accumulations of microplastic on shorelines worldwide: sources and sinks. *Environ. Sci.*
306 *Technol.* **2011**, *45*, 9175-9179.
- 307 2. Law, K. L.; Moret-Ferguson, S.; Maximenko, N. A.; Proskurowski, G.; Peacock, E. E.;
308 Hafner, J.; Reddy, C. M. Plastic Accumulation in the North Atlantic Subtropical Gyre. *Science*
309 **2010**, *329*, 1185-1188.
- 310 3. Goldberg, E. D. Plasticizing the seafloor: An overview. *Environ. Technol.* **1997**, *18*, 195-201.
- 311 4. Hirai, H.; Takada, H.; Ogata, Y.; Yamashita, R.; Mizukawa, K.; Saha, M.; Kwan, C.; Moore,
312 C.; Gray, H.; Laursen, D.; Zettler, E.; Farrington, J.; Reddy, C.; Peacock, E.; Ward, M. Organic

313 micropollutants in marine plastic debris from the open ocean and remote and urban beaches.
314 *Mar. Pollut. Bull.* **2011**, *62*, 1683-1692.

315 5. Rochman, C. M.; Browne, M. A.; Halpern, B. S.; Hentschel, B. T.; Hoh, E.; Karapanagioti, H.
316 K.; Rios-Mendoza, L. M.; Takada, H.; Teh, S.; Thompson, R. C. Classify plastic waste as
317 hazardous. *Nature* **2013**, *494*, 169-171.

318 6. Rochman, C. M.; Hoh, E.; Hentschel, B. T.; Kaye, S. Long-term field measurement of
319 sorption of organic contaminants to five types of plastic pellets: Implications for plastic marine
320 debris. *Environ. Sci. Technol.* **2013**, *47*, 1646-1654.

321 7. Rochman C. M. Plastics and priority pollutants: a multiple stressor in aquatic habitats.
322 *Environ. Sci. Technol.* **2013**, *47*, 2439-2440.

323 8. Van, A.; Rochman, C. M.; Flores, E. M.; Hill, K. L.; Vargas, E.; Vargas, S. A.; Hoh, E.,
324 Persistent organic pollutants in plastic marine debris found on beaches in San Diego, California.
325 *Chemosphere* **2012**, *86* (3), 258-263.

326 9. Lima, A. L. C.; Farrington, J. W.; Reddy, C. M., Combustion-Derived Polycyclic Aromatic
327 Hydrocarbons in the Environment—A Review. *Environ. Forensics* **2005**, *6* (2), 109-131.

328 10. Harvey, R. G., Environmental Chemistry of PAHs. In *PAHs and Related Compounds-*
329 *Chemistry*, Nielson, A. H., Ed.; Springer: New York, 1998; Vol. 3.1.

330 11. Horii, Y.; Ok, G.; Ohura, T.; Kannan, K., Occurrence and Profiles of Chlorinated and
331 Brominated Polycyclic Aromatic Hydrocarbons in Waste Incinerators. *Environ. Sci. Technol.*
2008, *42*, 1904-1909.

330 12. Ma, J.; Horii, Y.; Cheng, J.; Wang, W.; Wu, Q.; Ohura, T.; Kannan, K., Chlorinated and
331 Parent Polycyclic Aromatic Hydrocarbons in environmental Samples from an Electronic Waste

- 332 Recycling Facility and a Chemical Industrial Complex in China. *Environ. Sci. Technol.* **2009**, *43*,
333 643-649.
- 334 13. Lima, A. L. C.; Farrington, J. W.; Reddy, C. M. Combustion-derived polycyclic aromatic
335 hydrocarbons in the environment—a review. *Environ. Forensics*, **2005**, *6*(2), 109-131.
- 336 14. Lohmann, R. Critical review of low-density polyethylene's partitioning and diffusion
337 coefficients for trace organic contaminants and implications for its use as a passive sampler.
338 *Environ. Sci. Technol.* **2012**, *46*, 606-618.
- 339 15. Dmitrienko, S. G.; Gurariy, E. Y.; Nosov, R. E.; Zolotoz, Y. A. Solid-phase extraction of
340 polycyclic aromatic hydrocarbons from aqueous samples using polyurethane foams in
341 connection with solid-matrix spectrofluorimetry. *Anal. Lett.* **2001**, *34*, 425-438.
- 342 16. PlasticsEurope, Plastics—the Facts 2012: An analysis of European plastics production,
343 demand and waste data for 2011. [http://www.plasticseurope.org/Document/plastics-the-facts-](http://www.plasticseurope.org/Document/plastics-the-facts-2012.aspx?FolID=2)
344 [2012.aspx?FolID=2](http://www.plasticseurope.org/Document/plastics-the-facts-2012.aspx?FolID=2)
- 345 17. Manzano, C.; Hoh, E.; Simonich, S. L. M., Improved Separation of Complex Polycyclic
346 Aromatic Hydrocarbon Mixtures Using Novel Column Combinations in GC × GC/ToF-MS.
347 *Environ. Sci. Technol.* **2012**, *46* (14), 7677-7684.
- 348 18. Pruter, A. T. Sources, quantities and distribution of persistent plastics in the marine
349 environment. *Mar. Pollut. Bull.* **1987**, *18*, 305-310.
- 350 19. Carpenter, E.; Anderson, S.; Harvey, G.; Miklas, H.; Peck, B. Polystyrene spherules in
351 coastal waters. *Science* **1972**, *178*, 749-750.
- 352 20. Lithner, D.; Larsson, A.; Dave, G. Environmental and health hazard ranking and assessment
353 of plastic polymers based on chemical composition. *Sci. Total Environ.* **2011**, *409*, 3309-3324.

- 354 21. Kitazawa, A.; Amagai, T.; Ohura, T., Temporal Trends and Relationships of Particulate
355 Chlorinated Polycyclic Aromatic Hydrocarbons and Their Parent Compounds in Urban Air.
356 *Environ. Sci. Technol.* **2006**, *40*, 4592-4598.
- 357 22. Ohura, T.; Kitazawa, A.; Amagai, T.; Makino, M., Occurrence, Profiles and Photoestabilities
358 of Chlorinated Polycyclic Aromatic Hydrocarbons Associated with Particulates in Urban Air.
359 *Environ. Sci. Technol.* **2005**, *39*, 85-91.
23. Wang, W.; Jariyasopit, N.; Schrlau, J.; Jia, Y.; Tao, S.; Yu, T.-W.; Dashwood, R. H.; Zhang,
W.; Wang, X.; Simonich, S. L. M., Concentration and Photochemistry of PAHs, NPAHs, and
OPAHs and Toxicity of PM_{2.5} during the Beijing Olympic Games. *Environ. Sci. Technol.* **2011**,
45 (16), 6887-6895.
- 360 24. Manzano, C.; Hoh, E.; Simonich, S. L. M., Quantification of Complex Polycyclic Aromatic
361 Hydrocarbon Mixtures in Standard Reference Materials Using Comprehensive Two-dimensional
362 Gas Chromatography with Time-of-flight Mass Spectrometry. *J Chrom A.* **2013**, Online
363 publication complete: 8-AUG-2013 DOI information: 10.1016/j.chroma.2013.07.093
- 364 25. Allan, I. J.; Booij, K.; Paschke, A.; Vrana, B.; Mills, G. A.; Greenwood, R. Field
365 performance of seven passive sampling devices for monitoring hydrophobic substances. *Environ.*
366 *Sci. Technol.* **2009**, *43*, 5383-5390.
- 367 26. Schrap, S. M.; Sleijpen, G. L. G.; Seinen, W.; Opperhuizen, A. Sorption kinetics of
368 chlorinated hydrophobic organic chemicals, Part II. *Environ. Sci. & Pollut. Res.* **1994**, *1*(2), 81-
369 92.
- 370 27. Ravindra, K.; Sokhi, R.; Van Grieken, R., Atmospheric polycyclic aromatic hydrocarbons:
371 Source attribution, emission factors and regulation. *Atmospheric Environment* **2008**, *42* (13),
372 2895-2921.

373 28. Robinson, A. L.; Donahue, N. M.; Rogge, W. F., Photochemical oxidation and changes in
374 molecular composition of organic aerosol in the regional context. *J. Geophys. Res.* **2006a**, *111*
375 (D3), D03302.

376 29. Robinson, A. L.; Subramanian, R.; Donahue, N. M.; Rogge, W. F., Source Apportionment of
377 Molecular Markers and Organic Aerosol1. Polycyclic Aromatic Hydrocarbons and Methodology
378 for Data Visualization. *Environ. Sci. & Technol.* **2006b**, *40* (24), 7803-7810.

379 30. Rogge, W. F.; Hildemann, L. M.; Mazurek, M. A.; Cass, G. R.; Simoneit, B. R. T., Sources
380 of fine organic aerosol. 2. Noncatalyst and catalyst-equipped automobiles and heavy-duty diesel
381 trucks. *Environ. Sci. & Technol.* **1993**, *27* (4), 636-651.

382 31. Guo, H.; Lee, S. C.; Ho, K. F.; Wang, X. M.; Zou, S. C., Particle-associated polycyclic
383 aromatic hydrocarbons in urban air of Hong Kong. *Atmos. Environ.* **2003**, *37* (38), 5307-5317.

384 32. Park, S. S.; Kim, Y. J.; Kang, C. H., Atmospheric polycyclic aromatic hydrocarbons in
385 Seoul, Korea. *Atmos. Environ.* **2002**, *36* (17), 2917-2924.

386 33. Sofowote, U. M.; Allan, L. M.; McCarry, B. E., Evaluation of PAH diagnostic ratios as
387 source apportionment tools for air particulates collected in an urban-industrial environment. *J.*
388 *Environ. Monitor.* **2010**, *12* (2), 417-424.

389 34. Soclo, H. H.; Garrigues, P. H.; Ewald, M. Origin of polycyclic aromatic hydrocarbons (PAHs)
390 in coastal marine sediments: case studies in Cotonou (Benin) and Aquitaine (France) areas. *Mar.*
391 *Pollut. Bull.* **2000**, *40*(5), 387-396.

392 35. Dickhut, R. M.; Canuel, E. A.; Gustafson, K. E.; Liu, K.; Arzayus, K. M.; Walker, S. E.;
393 Edgecombe, G.; Gaylor, M. O.; MacDonald, E. H. Automotive sources of carcinogenic
394 polycyclic aromatic hydrocarbons associated with particulate matter in the Chesapeake Bay
395 Region. *Environ. Sci. Technol.* **2000**, *34*, 4635-4640.

- 396 36. Sienna, M. Oxygenated polycyclic aromatic hydrocarbons in urban air particulate matter.
397 *Atmos. Environ.* **2006** 40(13), 2374-2384.
- 398 37. Hughes, W. B.; Holba, A. G.; & Dzou, L. I. The ratios of dibenzothiophene to phenanthrene
399 and pristane to phytane as indicators of depositional environment and lithology of petroleum
400 source rocks. *Geochim. Cosmochim. Ac.* **1995**, 59(17), 3581-3598.
- 401 38. Durlak, S. K.; Biswas, P.; Shi, J.; Bernhard, M. J., Characterization of Polycyclic Aromatic
402 Hydrocarbon Particulate and Gaseous Emissions from Polystyrene Combustion. *Environmental*
403 *Science & Technology* **1998**, 32 (15), 2301-2307.
- 404 39. Zabaniotou, A.; Kassidi, E. Life cycle assessment applied to egg packaging made from
405 polystyrene and recycled paper. *J. Cleaner Production.* **2003** 11(5), 549-559.
- 406 40. Kwon, E.; Castaldi, M. J. Investigation of mechanisms of polycyclic aromatic hydrocarbons
407 (PAHs) initiated from the thermal degradation of styrene butadiene rubber (SBR) in N₂
408 atmosphere. *Environ. Sci. Technol.* **2008**, 42, 2175-2180.
- 409 41. Wheatley, L.; Levendis, Y. A.; Vouros, P. Exploratory study on the combustion and PAH
410 emissions of selected municipal waste plastics. *Environ. Sci. Technol.* **1993**, 27, 2885-2895.
- 411 42. Muller, J. F.; Manomanii, K., Mortimer, M. R.; McLachlan, M. S. Partitioning of polycyclic
412 aromatic hydrocarbons in the polyethylene/water system. *Fresenius J. Anal. Chem.* **2001**, 371,
413 816-822.
- 414 43. Pascall, M. A.; Zabik, M. E.; Zabik, M. J.; Hernandez, R. J. Uptake of polychlorinated
415 biphenyls (PCBs) from an aqueous medium by polyethylene, polyvinyl chloride, and polystyrene
416 films. *J. Agr. Food Chem.* **2005**, 53, 164-169.
- 417 44. Kirk, R. E.; Othmer, D. F.; Mark, H. F., *Encyclopedia of chemical technology*. Interscience
418 Publishers: 1965; Vol. 6.

419 45. Lo, M. T., Sandi, E. Polycyclic aromatic hydrocarbons (polynuclears) in foods. In *Residue*
420 *reviews*. Springer New York, 1978; pp. 35-86.

421 46. Huck, C. W.; Bonn, G. K. Recent developments in polymer-based sorbents for solid-phase
422 extraction. *J. Chromatog. A.* **2000** 885(1), 51-72.

423 47. Penner, N. A.; Nesterenko, P. N.; Ilyin, M. M.; Tsyurupa, M. P.; & Davankov, V. A.
424 Investigation of the properties of hypercrosslinked polystyrene as a stationary phase for high-
425 performance liquid chromatography. *Chromatographia.* **1999** 50(9-10), 611-620.

426 48. Kartar, S., Abou-Seedo, F., Sainsbury, M. Polystyrene spherules in the Severn estuary—a
427 progress report. *Mar. Pollut. Bull.* **7**, 52 (1976).

428

429 **Supplementary Materials** Table S1 shows GC×GC/ToF-MS optimized parameters, Table S2
430 shows the list of PAHs targeted by GC×GC/ToF-MS, Table S3a and S3b shows the percent
431 distribution of PAHs on PS at Harbor Excursion and Shelter Island, Figure S1 shows a map of
432 our study sites in SD Bay, Figure S2 shows time trends for MPAHs, OPAHs and SPAHs over
433 time, Figure S3 shows PPAHs over time and Figure S4 shows total PPAHs over time for each of
434 the 6 major polymer types. This information is available free of charge via the Internet at
435 <http://pubs.acs.org/>.

436 **Acknowledgements:** This material is based on work supported by SoCal SETAC, PADI
437 Foundation, SDSU Division of Research Affairs, National Science Foundation Grant No.
438 0548190, and a National Science Foundation Graduate Research Fellowship (Grant No.
439 2010101195). This publication was made possible in part by grant number P30ES00210 from the
440 National Institute of Environmental Health Sciences (NIEHS), NIH and NIEHS Grant P42
441 ES016465, and the National Science Foundation (ATM-0841165). The American Chemistry
442 Council donated virgin plastic pellets. We thank Harbor Excursion and Michelson Yachts at
443 Shelter Island for donating dock space. S. Kaye and M. Oei assisted with chemical analyses, and
444 Z. Schakner, S. Wheeler, M. Colvin, C. Mazloff, J. Barr, M. Moore and S. Celustka assisted in
445 the field. We thank K. Watanabe for assistance with Figure S1, G. Cherr for advising on
446 experimental design and A. J. Underwood for advice regarding statistical analyses. The authors
447 thank the analytical chemistry core of OSU's Superfund Research Program for supplying
448 standards and Prof. Takeshi Ohura at the University of Shizouka in Shizouka, Japan for
449 supplying C1PAH and BrPAH standards. Its contents are solely responsibility of the authors and
450 do not necessarily represent the official view of NIEHS, NIH. The authors declare no conflicts of
451 interest.

Table 1: Concentration of PAHs found in PS pellets (in ng/g) deployed for 0, 1, 3, 6, 9 and 12 months in Harbor Excursion and Shelter Island sampling sites, determined using GC×GC/ToF-MS.

months	0 (blank)		Harbor Excursion									Shelter Island										
	n=3	SD	1 month	3 months	6 months	9 months	12 months	1 month	3 months	6 months	9 months	12 months	1 month	3 months	6 months	9 months	12 months					
			n=2	n=2	n=2	n=2	n=2	n=2	n=2	n=2	n=2	n=2	n=2	n=2	n=2	n=2	n=2					
1,3-Dimethylnaphthalene	24.3	4.24	29.8	17.9	22.9	23.1	15.4	22.3	18.2	17.4	17.8	14.8	18.5	21.7	17.0	17.8	14.9	14.8	9.64	12.3	13.4	8.93
1-Methylphenanthrene	12.2	0.18	29.2	16.6	17.2	16.0	16.4	15.1	19.3	16.9	18.1	17.1	13.2	13.9	13.4	13.6	14.5	12.7	14.5	12.9	13.4	13.7
1-Methylpyrene	n.d.	0	17.6	16.2	16.3	21.0	15.6	14.9	17.5	18.1	16.3	17.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,6-Dimethylnaphthalene	9.30	0.5	8.33	6.67	6.73	7.33	6.56	8.21	6.83	6.26	6.94	6.92	7.45	7.98	6.51	6.90	6.30	6.04	6.30	5.67	5.97	5.75
2-Methylantracene	n.d.	0	17.0	18.4	17.3	16.7	17.9	15.8	18.9	18.7	18.1	18.9	13.8	14.1	13.9	13.9	15.2	13.7	15.1	14.5	14.9	15.0
2-Methylphenanthrene	13.5	0.15	19.7	15.5	15.6	15.5	15.1	14.5	14.9	15.9	15.8	15.3	13.9	14.0	14.1	13.9	14.2	13.4	14.4	13.4	13.9	13.8
Triphenylene	n.d.	0	10.9	8.60	8.63	7.56	8.82	6.32	9.23	9.68	8.09	10.2	5.84	5.41	5.38	5.59	6.33	5.65	6.32	5.65	6.53	6.71
ΣMPAHs	59.2	4.71	132	99.9	105	107	95.9	97.1	105	103	101	101	72.6	77.1	70.3	71.7	71.4	66.1	66.3	64.4	68.1	63.9
Acenaphthene	5.23	0.49	38.7	13.3	13.5	14.8	14.6	13.2	15.2	14.2	15.5	14.0	5.40	5.66	6.19	5.93	5.73	5.45	6.21	5.41	5.81	5.96
Acenaphthylene	6.76	0.83	18.7	19.3	15.8	17.8	22.8	13.9	18.8	22.8	18.7	22.1	9.33	9.74	9.80	10.4	11.2	10.3	15.2	10.6	11.1	13.3
Anthracene	5.41	0.14	44.1	42.2	40.1	39.2	43.8	25.4	45.9	53.5	44.3	49.4	10.1	10.6	11.0	13.7	15.6	14.3	18.1	13.5	16.7	18.1
Benz[a]anthracene	n.d.	n.d.	34.2	21.2	17.6	17.1	18.9	12.5	21.2	18.3	16.0	19.6	6.08	6.95	6.32	7.29	8.51	6.73	8.67	7.51	7.85	9.91
Benzo[a]pyrene	n.d.	n.d.	24.0	21.4	18.9	19.2	17.1	13.5	16.6	24.7	16.1	18.2	6.42	7.76	7.17	8.32	9.48	7.58	11.3	8.99	9.62	10.3
Benzo[b]fluoranthene	n.d.	n.d.	33.0	35.0	44.2	35.0	38.8	22.6	35.7	40.0	27.7	31.5	12.0	13.5	13.8	15.0	19.0	15.4	18.6	18.1	16.6	22.1
Benzo[e]pyrene	n.d.	n.d.	24.9	25.1	22.8	23.1	25.2	14.5	22.0	33.6	20.7	22.6	8.78	9.41	9.32	10.7	12.6	10.3	13.7	14.5	11.7	14.9
Benzo[ghi]perylene	n.d.	n.d.	n.d.	38.0	36.6	36.3	40.0	33.6	38.6	41.9	37.9	37.5	34.3	34.2	34.8	33.8	35.5	33.1	34.9	34.8	34.4	34.6
Benzo[k]fluoranthene	n.d.	n.d.	21.7	23.3	27.9	23.2	23.1	15.9	21.7	23.3	17.4	20.2	9.43	8.73	8.54	10.6	11.9	10.2	11.3	10.6	10.8	11.9
Chrysene	n.d.	n.d.	33.9	20.9	18.7	20.0	19.2	11.7	22.0	23.6	15.4	23.5	7.45	7.30	7.50	7.72	9.25	7.49	9.09	7.55	8.36	11.8
Fluoranthene	23.0	13.6	126	33.2	41.6	35.2	39.4	24.8	46.4	36.0	33.5	43.9	18.4	19.5	18.3	19.4	21.7	18.2	25.7	21.3	23.0	26.1
Fluorene	25.4	3.41	74.0	40.1	48.3	54.1	37.2	43.2	38.8	43.1	47.1	46.5	31.6	36.8	25.6	38.9	31.5	34.9	40.6	32.1	24.0	30.1
Indeno[1,2,3-cd]pyrene	n.d.	n.d.	30.4	33.7	33.8	32.6	34.3	27.7	33.2	39.6	32.9	32.4	27.6	28.4	27.9	29.8	30.6	27.9	28.0	29.2	29.8	30.7
Phenanthrene	12.6	0.64	208	74.2	68.9	70.8	67.1	105	96.4	141	96.9	113	63.0	71.1	85.8	126	133	127	82.3	89.6	98.4	109
Pyrene	15.7	6.42	203	55.5	74.6	59.5	68.3	21.0	73.0	57.5	58.9	68.4	17.8	22.0	14.5	15.1	22.9	17.7	13.6	20.2	17.4	27.6
ΣPPAHs	94.2	14.5	915	496	523	498	510	398	545	613	499	563	268	292	286	353	378	347	337	324	325	376
9-Fluorenone	7.90	1.2	10.0	10.1	10.5	11.2	9.08	10.5	10.8	10.6	12.9	12.0	9.63	10.9	9.47	9.64	12.0	9.83	11.0	8.97	9.11	11.1
1,4-Naphthoquinone	45.4	0.79	47.0	45.9	47.8	47.5	46.6	45.8	47.4	48.0	48.7	47.8	46.9	46.7	45.6	46.7	46.9	44.0	48.8	46.0	46.5	51.1
ΣOPAHs	53.3	1.93	57.0	56.0	58.3	58.7	55.7	56.3	58.2	58.6	61.6	59.8	56.5	57.6	55.1	56.3	58.9	53.9	59.8	54.9	55.6	62.2
Dibenzothiophene	4.35	0.06	19.3	6.90	7.41	7.30	6.19	5.99	7.40	6.92	7.13	7.02	3.98	3.99	3.87	4.01	4.08	3.92	4.15	3.93	3.97	4.03
ΣSPAHs	4.35	0.06	19.3	6.90	7.41	7.30	6.19	5.99	7.40	6.92	7.13	7.02	3.98	3.99	3.87	4.01	4.08	3.92	4.15	3.93	3.97	4.03
Total PAHs	211.0	21	1123	659	694	671	667	558	716	782	669	730	401	430	416	485	512	470	468	447	453	506

n.d.: compound not detected

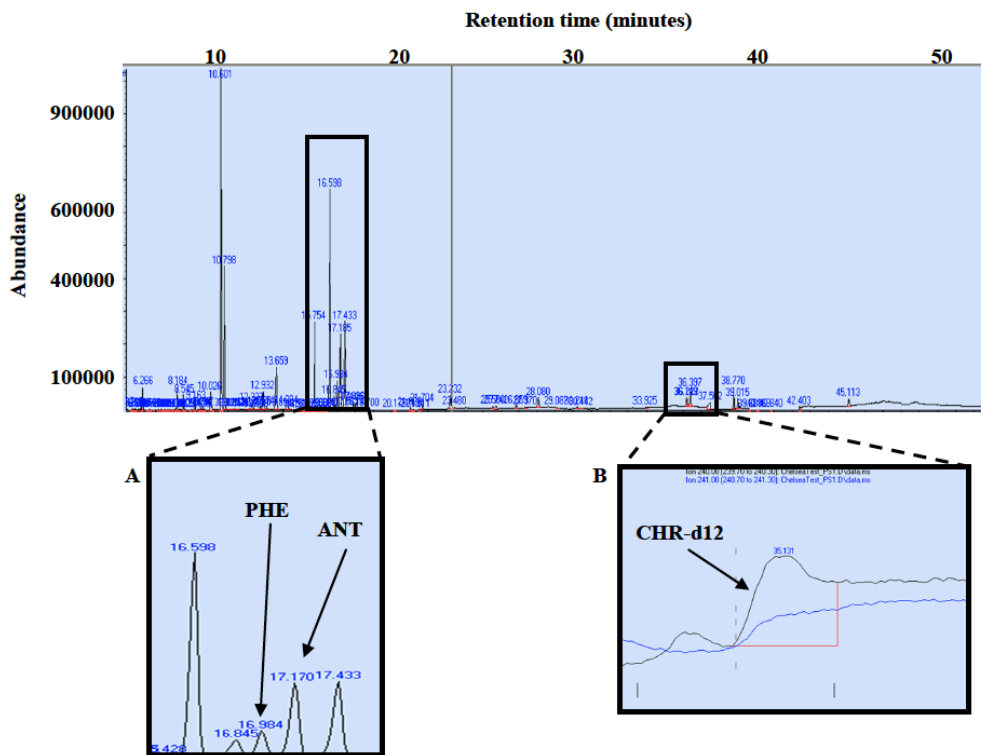


Figure 1: One-dimensional chromatogram of the sum of selected ions for a polystyrene extract analyzed using a 30 m DB-5 column after solid phase extraction (SPE). The inner boxes show some of the PAHs with co-elution problems. (A) Phenanthrene (PHE) and anthracene (ANT) co-eluting with interfering components represented by large peaks that do not correspond to PAHs or internal standards. (B) Chrys-ene-d12 (CHR-d12) showing peak broadening and baseline drifting possibly due to matrix co-eluting with target compound.

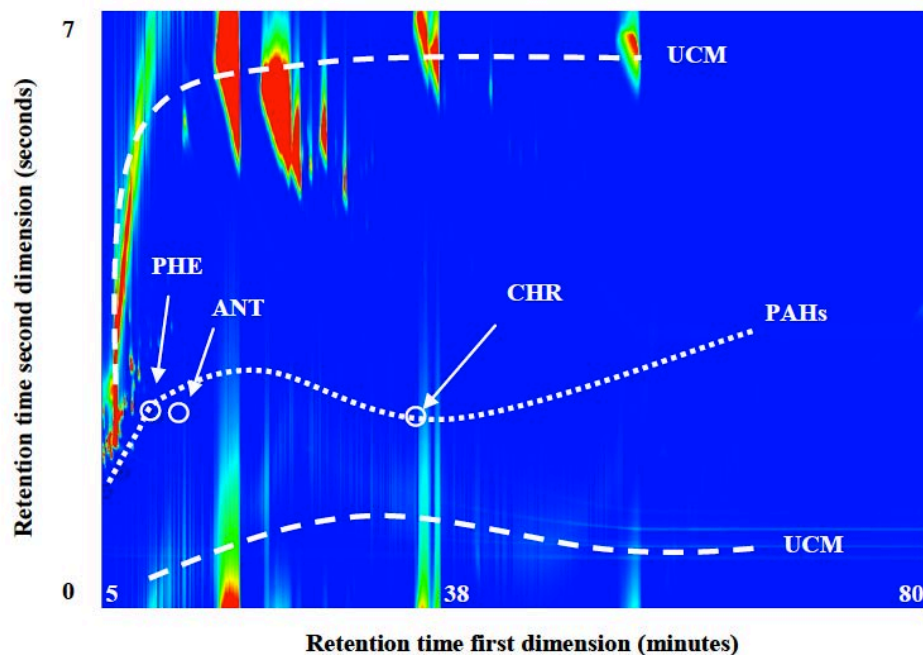


Figure 2: GC×GC/ToF-MS contour map of the total ion chromatogram (TIC) for a PS extract. The *x*-axis represents the retention time in the first dimension (min) and the *y*-axis the retention time in the second dimension (s). The dotted line represents the elution profile for the PAHs in the sample, which is isolated from most of sample matrix and UCM, represented by the dashed line below and above the PAHs line. PAHs that had co-elution problems when using a one-dimensional GC are labeled, phenanthrene (PHE), anthracene (ANT) and chrysene (CHR).

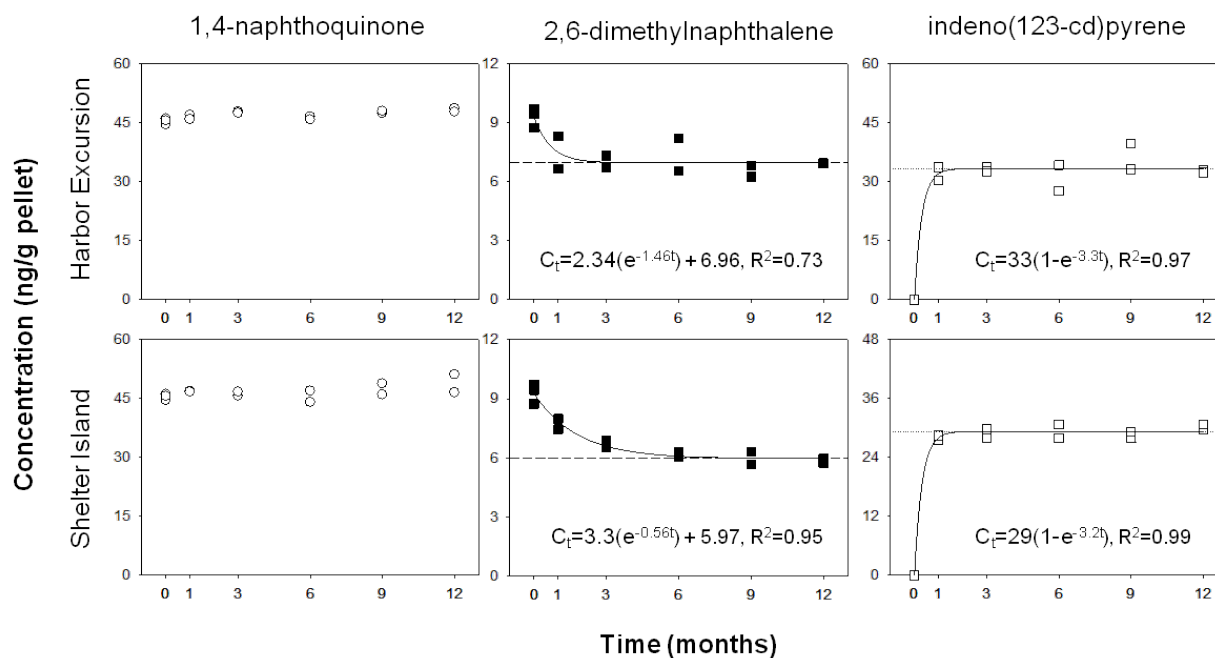
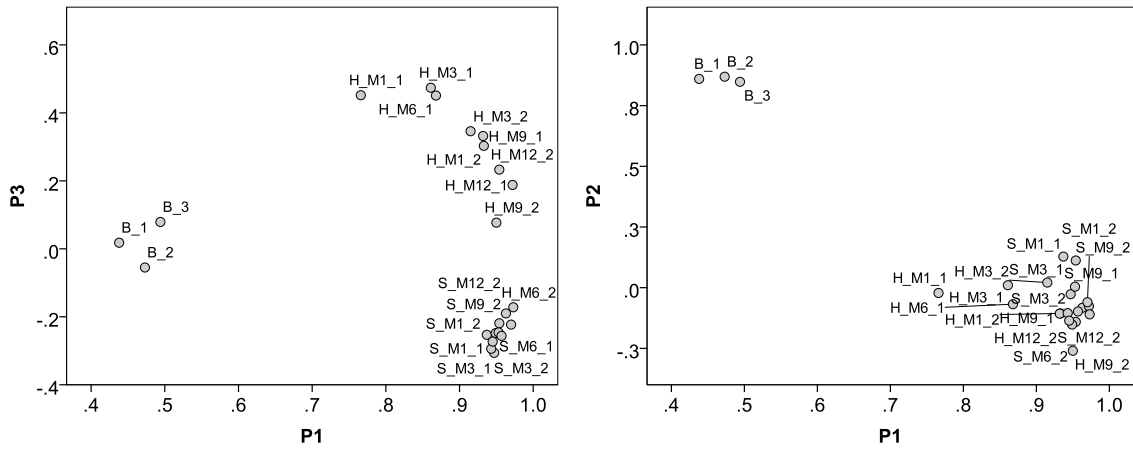


Figure 3. Concentrations of 1,4-naphthoquinone (no change over time; left), 2,6-dimethylnaphthalene (decreasing over time; middle), indeno(123-cd)pyrene (increasing over time; right) in ng/g of pellets vs. time for PS at Harbor Excursion (top rows) and Shelter Island (bottom rows). Please note that vertical axes differ among graphs. Data were fit to the first-order approach to equilibrium model²⁵ using the exponential rise to maximum equation $C_t = C_{eq}(1 - e^{-kt})$ or the exponential decay model²⁶ using the equation $C_t = (C_0 - C_{eq})e^{-kt} + C_{eq}$, where C_t is the concentration at time t , C_{eq} is the predicted equilibrium concentration, C_0 is the initial concentration and k is the rate constant. The horizontal dotted line denotes the predicted C_{eq} for each plastic type. Where the equation and lines are missing, the data could not be fit to the equation.

452

453



454

Figure 4: Principal component analysis of the concentration of PAHs. Three principal components are shown. Generalized grouping: B – blank, virgin PS pellets not deployed, H_M – Harbor Excursion sampling site, with 1, 3, 6, 9 and 12 months of exposure, and S_M – Shelter Island sampling site, with 1, 3, 6, 9 and 12 months of exposure

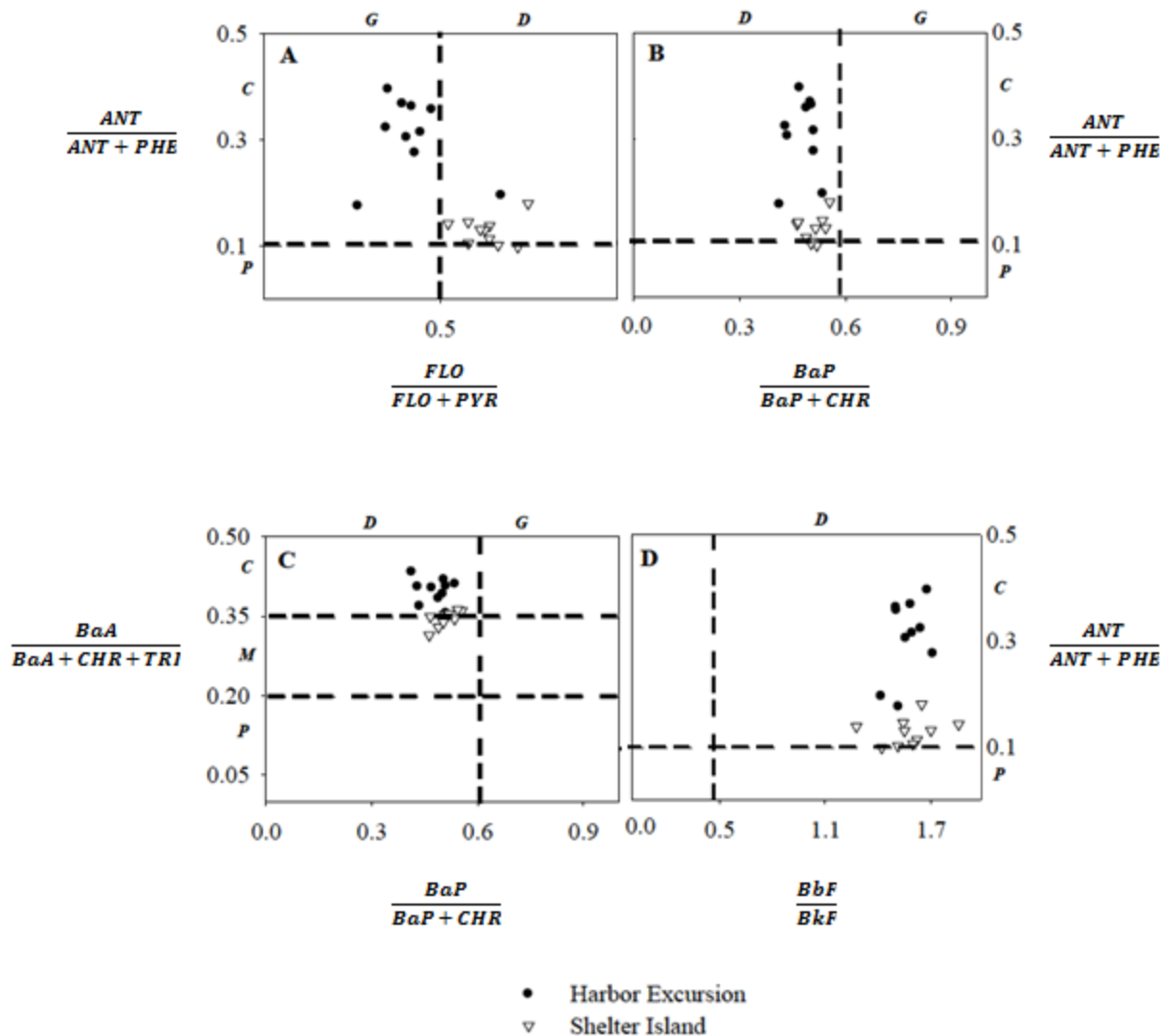


Figure 5: Bi-variate plots of PAH diagnostic ratios for PS pellets deployed in both sampling sites. (A) $FLO/(FLO+PYR)$ vs. $ANT/(ANT+PHE)$, (B) $BaP/(BaP+CHR)$ vs. $ANT/(ANT+PHE)$, (C) $BaP/(BaP+CHR)$ vs. $BaA/(BaA+CHR+TRI)$, (D) BbF/BkF vs. $ANT/(ANT+PHE)$. Dashed lines represent threshold values and letters in italics represent possible sources: *G* = gasoline, *D* = diesel, *C* = combustion of petroleum derivatives, *P* = PAHs from petroleum, *M* = mix sources.

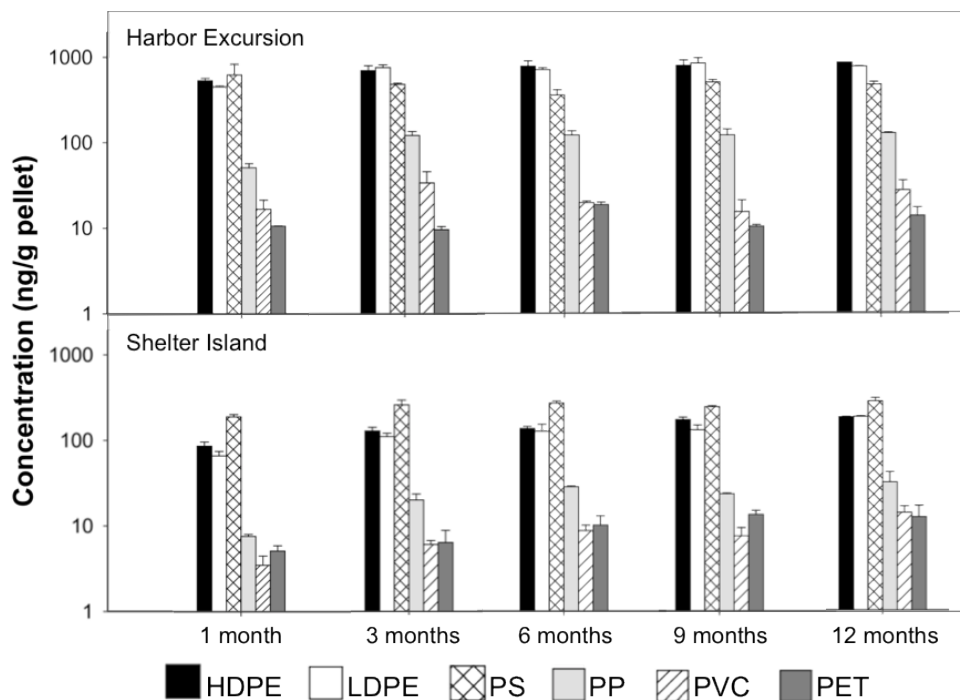


Figure 6: Mean concentrations (\pm S.E.) of Σ PPAHs (ng/g) sorbed to each plastic type at each location during each sampling period (1, 3, 6, 9 and 12 months; $n=2$). Harbor Excursion (HE-site) is shown on the top and Shelter Island (SI-site) on the bottom. At each sampling period, 2-factor ANOVA showed significant differences among plastic types ($p<0.001$) and locations ($p<0.001$), and post-hoc Tukey comparisons consistently distinguished HDPE, LDPE and PS as a group of plastics with the largest PPAH concentrations and PET and PVC with the smallest PPAH concentrations.