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Application of passive sampling for measuring dissolved concentrations of organic contaminants in the water column at three marine superfund sites

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2

3 **Passive Sampler C_{free} Measurements at Superfund Sites**

4

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14 **Application of Passive Sampling for Measuring Dissolved Concentrations (C_{free}) of Organic**
15 **Contaminants in the Water Column at Three Marine Superfund Sites**

16

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73 **Abstract**

74 Historically, acquiring the freely dissolved concentration (C_{free}) of HOCs has been challenging.
75 In recent years, passive sampling has been demonstrated to be an effective tool for determining
76 C_{free} in the water column and in sediment interstitial waters. Currently, there is an effort
77 underway encouraging remedial project managers (RPMs) at contaminated sites to use passive
78 sampling to collect C_{free} data in order to improve site assessments. The objective of this
79 investigation was to evaluate the use of passive sampling for measuring water column C_{free} for
80 several HOCs at three U.S. EPA Superfund sites. Sites investigated included New Bedford
81 Harbor, Palos Verdes Shelf and Naval Station Newport and the passive samplers evaluated were
82 polyethylene (PE), polydimethylsiloxane (PDMS) coated solid phase microextraction (SPME)
83 fibers, semi-permeable membrane devices (SPMD), and polyoxymethylene (POM). In general,
84 the different passive samplers demonstrated good agreement with C_{free} values varying by a factor
85 of two to three. Further, at New Bedford Harbor, where conventional water sample
86 concentrations were also measured (i.e., grab samples), passive sampler-based C_{free} agreed within
87 a factor of two. These findings suggest that all of the samplers were experiencing and measuring
88 similar C_{free} during their respective deployments. Also, at New Bedford Harbor, a strong log-
89 linear, correlative and predictive relationship was found between PE passive sampler
90 accumulation and (lipid-normalized blue mussel bioaccumulation of PCBs ($r^2 = 0.92$; $p \lll 0.05$)). This evaluation demonstrates the utility of passive sampling for generating scientifically
92 accurate water column C_{free} which is critical for making informed environmental management
93 decisions at contaminated sediment sites.

94

95 **Key Words:** Passive sampling, Superfund, Bioavailability, C_{free} , Polyethylene (PE),
96 Polyoxymethylene (POM), Solid phase microextraction (SPME), Semi-permeable membrane
97 devices (SPMD)

98 **Introduction**

99 Studies over the last few decades have demonstrated that many aquatic organisms
100 including fish and wildlife are exposed to anthropogenic contaminants present in the water
101 column that originate from contaminated sediments [1, 2]. Consequently, to accurately and
102 holistically assess exposures at contaminated sediment sites, including U.S. EPA Superfund
103 sites, it is critical to measure the water column concentrations directly. The exposure of aquatic
104 organisms to hydrophobic organic chemicals (HOCs) like polychlorinated biphenyls (PCBs),
105 polycyclic aromatic hydrocarbons (PAHs), polybrominated diphenylethers (PBDEs),
106 polychlorinated dibenzo-p-dioxins and dibenzofurans, and chlorinated pesticides in the water
107 column is most strongly correlated to the freely dissolved concentration (C_{free}) while uptake from
108 environmental sorptive phases like colloids or suspended particles is often limited [3, 4].
109 Consequently, C_{free} is considered a strong surrogate measurement for the bioavailable
110 concentrations of many HOCs. However, measuring the C_{free} in the water column in the field
111 remains technically challenging because of the relatively low concentrations of contaminants,
112 potential for contamination from the sorptive phases, and losses to collection gear. Several
113 recently developed passive sampling methods selectively measure C_{free} for HOCs [5] including
114 polyethylene and triolein-based semipermeable membrane devices (SPMDs) [6, 7],
115 polydimethylsiloxane (PDMS)-based solid phase microextraction (SPME) [8-10]
116 polyoxymethylene (POM) [11-13], and polyethylene (PE) [14-21].

117
118 All of these passive sampling methods use essentially the same approach for sampling
119 C_{free} . In this approach, contaminants partition between C_{free} (ng/L) in the aqueous phase and
120 some form of passive sampling absorptive carbon based polymer or liquid phase (C_{PS}) (ng/L):

121

122
$$C_{free} \leftrightarrow C_{PS} \quad [1]$$

123

124 Under equilibrium conditions, the relationship between the passive sampler phase and dissolved
125 phase can be expressed as a passive sampler-dissolved phase partition coefficient ($K_{PS-free}$) (L/L)
126 and used to estimate the C_{free} concentration of a given contaminant:

127
$$C_{free} = \frac{C_{PS}}{K_{PS-free}} \quad [2]$$

128 If equilibrium conditions cannot be assumed or demonstrated, Equation 2 can be adjusted to
129 estimate equilibrium concentrations using performance reference compounds (PRCs) similar in
130 physicochemical behavior to the target contaminants [17, 22]. The PRCs are introduced to the
131 passive sampler before deployment in the environment and partition into the aqueous phase at a
132 rate comparable to the partitioning of the target contaminants into the polymer. In principle,
133 with these techniques, only the C_{free} contaminants partition into the passive sampler. Therefore,
134 uptake of contaminants into the passive sampler reflects the bioavailable concentration and can
135 be compared to bioaccumulation by water column and sediment deployed biomonitoring
136 organisms (e.g., blue mussels, polychaetes) and/or used to estimate HOC C_{free} exposed to
137 organisms using Equation 2 [12, 16, 23-25]. This type of exposure information is very important
138 for understanding the direct exposure to water column organisms (e.g., fish) and serving as input
139 information for modelling bioaccumulation and assessing risk to human and ecological health
140 higher in the food chain (e.g., avians, wildlife). Therefore, to successfully predict exposures to
141 water column organisms and model higher level impacts it is critical to insure that measurements
142 of C_{free} are as accurate and scientifically-robust as possible.

143
144 In recent years, the use of passive sampling for measuring C_{free} at U.S. EPA Superfund
145 sites has been encouraged as a scientifically-robust tool for assessing exposure (e.g., [26-28])
146 and, in a limited number of cases, remedial project managers (RPMs) at Superfund sites have
147 applied passive sampling (e.g., [18, 19, 29]). To this end, the current investigation evaluates the
148 application of passive samplers at three U.S. EPA Superfund sites for measuring water column
149 C_{free} of target contaminants including PCBs, PAHs and PBDEs. The Superfund sites investigated
150 included New Bedford Harbor (NBH) (New Bedford, MA, USA), the Naval Station Newport
151 (NSN) (Newport, RI, USA), and Palos Verdes Shelf (PVS) (Los Angeles, CA, USA). Risk at
152 each of these sites is driven by concerns with human consumption of contaminated seafood as
153 well as adverse ecological effects due to exposure to dissolved concentrations of bioavailable
154 contaminants (i.e., C_{free}). In general, studies were designed to compare the performance of
155 different types of passive samplers (e.g., SPME, PE, POM, SPMD) to one another, and in some
156 cases, to biomonitoring organisms (e.g., blue mussels *Mytilus edulis*) under field conditions.
157 These studies also had regulatory objectives which included establishing baseline water column
158 C_{free} of target contaminants at the sites (e.g., NBH, NSN) and evaluating the feasibility of using

159 passive samplers at a deep water Superfund site (PVS). At the NBH Superfund site, water
160 column samples were also collected and extracted using conventional techniques (i.e., grab
161 sample with liquid-liquid extraction with organic solvents) and solid phase extraction (SPE) for
162 comparison to passive sampling-based findings. Results of this work are intended to encourage
163 RPMs at contaminated sediment sites to use passive sampling as an additional tool for making
164 informed environmental management decisions.

165

166 **Materials and Methods**

167 *Study Designs*

168 *New Bedford Harbor Superfund Site* To assess baseline water column concentrations of total
169 PCB C_{free} , two deployments were performed. Passive samplers were deployed at NBH2 and
170 NBH4 which are two long-term U.S. EPA monitoring locations (Table 1) (Supplemental Data
171 Figure S1). In each deployment, passive samplers were deployed in four temporal intervals:
172 days 0-7, days 0-14, days 0-21 and days 0-28 or 29 one meter above the sediment bed. Water
173 samples were also collected one meter above the sediment bed at the time of passive sampler
174 recovery. In the first study (fall), triplicate PE attached by stainless wire to the mooring lines
175 were deployed from 10 October 2007 to 7 November 2007 for a total of 28 days. For
176 comparative purposes, bagged blue mussels (*M. edulis*), also suspended one meter above the
177 bottom, were exposed for 33 days at stations NBH2 and NBH4 from 19 October 2007 to 21
178 November 2007. In the second deployment (winter), at each station, SPMD, SPME and PE were
179 deployed on triplicate moorings. On day 0 at each station, a total of 12 SPMD and SPME (in
180 canisters), and wire-attached PE passive samplers were deployed on individual moorings
181 (Supplemental Data Figure S2a). The monitoring period extended from 19 November 2007
182 through 18 December 2007 for a total of 29 days. Three SPMD and SPME containing canisters
183 and three PE polymer strips were recovered from the moorings on each of the four following
184 time periods: 7, 14, 21, and 29 days after deployment. As in the fall deployment, water samples
185 were also collected on a weekly basis.

186

187 *Palos Verdes Shelf Superfund Site* For this investigation, three to five month deployments were
188 performed at seven stations at depths ranging from 19 to 65 m (Table 1) (Supplemental Data
189 Figure S1) with PCBs as the target contaminant. To assess the effectiveness of passive sampling

190 at this deep water site, individual PE samplers were deployed, fastened using stainless steel wire,
191 to United States Geological Survey (USGS) acoustic Doppler current profilers resting on the
192 sediment surface (Supplemental Data Figure S2b). Samplers were attached 1.2 to 5.2 m above
193 the sediment surface often with multiple samplers on a given profiler (Table 1).

194

195 *Naval Station Newport Superfund* At this site, one deployment was performed at four stations
196 with PCBs, PAHs and PBDEs as the target contaminants (Table 1) (Supplemental Data Figure
197 S1). Two types of passive samplers, PE and POM, were deployed for 21 days in extended
198 minnow traps (Supplemental Data Figure S2c) to assess baseline C_{free} in the water column prior
199 to initiation of remediation of portions of the site. All samplers were deployed one meter above
200 the sediment surface. Additional information about each site is provided in the Supplemental
201 Data section.

202

203 *Passive Sampler Design, Deployment and Recovery*

204 For NBH deployments, SPMDs were composed of 91.4 cm long, 2.5 cm wide, lay flat,
205 hollow low-density polyethylene ribbons (70-95 μm thick) containing 1 mL pure (99%), high-
206 molecular weight lipid glyceryl trioleate (triolein) (Sigma-Aldrich, St Louis, MO, USA) in a thin
207 film. Prior to deployment, a PRC mixture containing chlorinated biphenyl (CB) 38 and CB50
208 was prepared in hexane at Battelle (Duxbury, MA, USA) and shipped to Environmental
209 Sampling Technologies, Inc. (EST) (St. Josephs, MO, USA). At EST, SPMD polyethylene
210 tubing was triple washed with optima grade hexane, injected with PRC-loaded triolein, and heat
211 sealed. Triolein had been amended with the PRC mixture for a final concentration of
212 approximately 25 ng/mL triolein each of CB38 and CB50. SPMDs were loaded onto stainless
213 steel deployment rigs (“spiders”), packed in air-tight, pre-cleaned aluminum containers, and
214 shipped to Battelle (Duxbury, MA, USA). Packages containing the SPMD deployment spiders
215 were stored at -4°C until the day of deployment. Spiders consisted of a stainless steel plate
216 equipped with a central hole and several Teflon or stainless steel posts. Canisters were deployed
217 in triplicate per deployment period and were constructed from stainless steel containing ports for
218 ample movement and circulation of the water column through the device.

219

220 For NBH deployments, disposable SPMEs consisted of 2.5 cm long pieces of optical
221 fiber with a 210 μm silica core and a 10 μm polydimethylsiloxane (PDMS) coating (equivalent
222 to 0.000173 mL PDMS) (Fiberguide, Stirling, NJ, USA). Prior to deployment, fibers and
223 protective stainless steel pouches (3 cm x 4 cm) were soaked in analytical grade methanol for at
224 least 10 minutes, dried at ambient temperatures, and wrapped in aluminum foil. Samplers were
225 then placed in storage containers (e.g., solvent-rinsed glass jars) and shipped to the site. Each
226 SPME replicate consisted of 15 or 30 fibers (total of 0.0026 or 0.0052 mL PDMS) per pouch
227 affixed to the top of the SPMD spider inside a canister using stainless steel wire and nylon zip
228 ties. There were three replicate SPMEs deployed at each station per deployment period. Upon
229 recovery, SPMD cannisters and SPME pouches were kept on ice, returned to the laboratory, and
230 stored at -4°C until extraction and chemical analysis.

231
232 All PE and POM samplers were pre-cleaned by soaking in acetone or hexane for 24 h and
233 then in dichloromethane (DCM) for 24 h. For NBH deployments, PEs were prepared from 51
234 μm thick, 30.5 cm long and 7.62 cm wide polyethylene film (1.19 mL PE) (Carlisle Plastics Inc.,
235 Minneapolis, MN, USA). Polyethylene was deployed in triplicate approximately one meter
236 above the sediment surface for each exposure interval using an anchor and flotation buoys. Prior
237 to deployment, these PEs were amended with PRCs in 80:20 methanol and deionized water
238 solution including 2,5-dibromobiphenyl (PBB), 2,2',5,5'-PBB, and 2,2',4,5,6-PBB at
239 approximately 21 ng/mL, 14 ng/mL, and 9.0 ng/mL PE, respectively, using methods described
240 by Booij et al. [22]. In addition, for a subset of NBH deployments, two thicknesses (i.e., 25 and
241 51 μm) (0.58 mL versus 1.19 mL PE) of PE were evaluated for assessing equilibrium. For the
242 Palos Verdes Shelf deployments, 50 cm long and 10 cm wide polyethylene PE strips (51 μm
243 thick) (2.55 mL) (Carlisle Plastics Inc., Minneapolis, MN, USA) were fastened using stainless
244 steel wire to the USGS acoustic Doppler current profilers. Prior to the deployments, as with the
245 NBH deployments, the same three PBBs and concentrations were used as PRCs. For Naval
246 Station Newport deployments, low-density PE (25 μm thickness; Covalence Plastics,
247 Minneapolis, MN, USA) and POM (75 μm ; CS Hyde Company, Milwaukee, IL, USA) were
248 prepared in 15 cm x 40 cm (1.5 mL PE) and 6 cm x 40 cm (1.8 mL POM) films, respectively.
249 Prior to deployments, PE and POM were amended with stable carbon PRCs including ^{13}C -CB28,
250 ^{13}C -CB52 and ^{13}C -CB138 in 80:20 methanol:water solutions for at least 21 days on an orbital

251 shaker using the methods described in Perron et al. [20]. Films of PE and POM were attached to
252 stainless steel wire (diameter = 0.081 cm; Malin Company, Cleveland, OH, USA) fastened inside
253 galvanized extended minnow traps (diameter = 22 cm, length = 76.2 cm) (Tackle Factory,
254 Fillmore, NY, USA). Inside each trap, three strips of PE and POM were arranged to maximize
255 their surface area. Samplers were deployed using an anchor and flotation buoys on a shore-
256 fastened mooring line. Upon recovery, all PE and POM films were immediately wrapped in pre-
257 cleaned metallic foil or placed in pre-cleaned glass jars, stored on ice or ice packs, and
258 transferred to the laboratory for storage at -4°C in the dark until extraction and analysis.

259

260 *Water Sample Collections*

261 At the NBH stations, discrete water samples (one liter) were collected in triplicate on a
262 weekly basis, following the retrieval/deployment of passive samplers during the fall and winter
263 deployments. Because of logistic issues, samples were not collected on Day 14 (3/12/07) in the
264 winter deployment. Water samples were collected using a 12-volt Teflon diaphragm pump, a
265 length of tygon tubing to reach the sampling depth (i.e., 1 m above the bottom) of the passive
266 sampling devices, and stored in clean glass containers. Following sample collection, the pump
267 and tubing were purged twice with DI water and one rinsate blank was collected. Samples were
268 placed on ice for transport to the laboratory. Once at the laboratory, water samples were filtered
269 through solvent-rinsed glass fiber filters (1 µm effective pore size) within 24 hours of collection.
270 As described in the Supplemental Data, water samples were analyzed and reported in two ways:
271 as “total” (i.e., dissolved and colloidal) and “C₁₈-based”. The C₁₈-based technique is an
272 alternative approach for measuring C_{free}. For discussion, these two measurements of PCB
273 concentrations will be referred to jointly as “aqueous” PCB measurements. Prior to extraction
274 and chemical analysis, the samples were stored at 4°C.

275

276 *Mussel Deployments*

277 For the fall NBH deployment, blue mussels (*M. edulis*) collected from clean sites in
278 coastal Sandwich (MA, USA) were selected by size (approximately 5-7 cm) and placed in mesh
279 plastic bags (approximately 25 mussels per bag). Deployments consisted of three to four
280 replicate bags exposed at each station positioned one meter above the bottom. After the 33 day

281 exposure, mussels were recovered, returned to the laboratory in coolers on ice, frozen at -4 °C,
282 and stored in the dark until chemical analysis.

283

284 *Chemical Analyses*

285 Passive samplers, tissues, and water samples were analyzed using gas
286 chromatography/mass spectroscopy (GC/MS) for selected PCBs, PAHs and PBDEs. Total PCBs
287 was defined as the sum of measured PCB congeners at each Superfund site: total PCB at New
288 Bedford Harbor, Palos Verdes Shelf and Naval Station Newport was the sum of 18, 29 and 26
289 congeners, respectively (Supplemental Data). Water samples from the NBH deployments were
290 also analyzed for dissolved organic carbon. Preparation, extraction and instrumental analysis is
291 described in the Supplemental Data section.

292

293 *Calculation of Passive Sampler-based Dissolved Concentrations (C_{free})*

294 When assuming equilibrium conditions, C_{free} was calculated using Equation 2. For non-
295 equilibrium conditions, C_{free} based on PE and POM deployments were calculated using PRC
296 with the following equation:

297

$$298 \quad C_{free} = \frac{C_{PS}}{(1 - e^{-k_e t}) * K_{PS-free}} \quad [3]$$

299 where, k_e is the PRC transfer coefficient (1/day) and t (day) the duration of the deployment:

300

$$301 \quad k_e = \frac{\ln \frac{C_{PRCi}}{C_{PRCf}}}{t} \quad [4]$$

302

303 and C_{PRCi} and C_{PRCf} are the initial and final concentrations (ng/g) in the polymer, respectively, of
304 the PRCs during the deployment. PRC % equilibration (i.e., $k_e * 100$) values were regressed
305 against PRC K_{OWs} to develop correlative relationships for estimating % equilibration values for
306 target contaminants. If target contaminant % equilibration values were less than 10%, the C_{free}
307 were not calculated because of insufficient evidence of equilibration of those compounds

308 between the polymer and environmental phases. Sources of partition coefficients for each type
309 of polymer used in this study are provided in the Supplemental Data.

310
311 For calculating C_{free} based on mussel bioaccumulation of PCBs, the lipid-water partition
312 coefficient ($K_{lipid-free}$) was derived for each PCB congener using the log $K_{lipid-free}$ to log K_{OW}
313 linear free energy relationship (LFER) reported by Schwarzenbach et al. [30] (i.e., $\log K_{lipid-free} =$
314 $0.91 \cdot \log K_{OW} + 0.5$). The C_{free} based on mussel lipid concentrations was calculated based on
315 Equation 7:

316
317
$$C_{free} = \frac{C_{lipid}}{K_{lipid-free}} \quad [5]$$

318
319 where, C_{lipid} is the lipid-normalized PCB concentration measured in the mussel tissues [5].

320
321 *Statistical Analyses*

322 Unless otherwise noted, the mean and one standard deviation of three replicates are reported for
323 passive sampler, water sample, DOC and mussel data. Statistical comparisons were performed
324 using analysis of variance (ANOVA) followed by protected least significant difference (LSD)
325 multiple comparison tests (SAS Institute, Cary, NC, USA) if more than two treatments were
326 being analyzed. Differences between treatments were considered as statistically significant using
327 an alpha (α) set at ≤ 0.05 .

328
329 **Results and Discussion**

330 *Comparison of C_{free} Measurements*

331 *New Bedford Harbor* During the fall deployments, total PCB C_{free} ranged from 25 ng/L to 360
332 ng/L for NBH4 and NBH2, respectively, based on PE measurements (Figure 1a). Aqueous
333 measurements of total PCB concentrations, based on the total water extractions and C_{18} -based
334 measurements, ranged from 21 to 120 ng/L at the same stations with total water extractions and
335 C_{18} -based measurements found to be similar (i.e., 5 to 18%). Further, PE-based C_{free} at NBH4
336 were relatively similar to the aqueous measurements; that is, within 20% while PE C_{free} were
337 three time larger than aqueous concentration at NBH2. Finally, mussel-based estimates of C_{free} ,

338 based on Equation 5, at NBH2 were also fairly similar to PE-based C_{free} , 400 ng/L versus 360
339 ng/L, while at station NBH4 mussels-based C_{free} , 58 ng/L, was about two times greater than PE-
340 based C_{free} (i.e., 25 ng/L). At NBH2, statistical analysis found mussel and PE C_{free} were not
341 significant different; similarly, water and C_{18} -based C_{free} values were also not significantly
342 different from one another. However, mussel C_{free} was significantly greater than C_{free} from the
343 other three treatments at NBH4. A more detailed comparison of mussel bioaccumulation and PE
344 accumulation of PCBs will be discussed later.

345
346 In the winter deployments, passive sampler-based total PCB C_{free} ranged from 76 to 170
347 ng/L and 7.7 to 31 ng/L at stations NBH2 and NBH4, respectively (Figure 1b). For comparison,
348 aqueous measurements of total PCBs ranged 53 to 97 ng/L and 16 to 30 ng/L at NBH2 and
349 NBH4, respectively. Within the passive sampler-based measurements of C_{free} , PE generated the
350 largest C_{free} values compared to SPME and SPMD. For example, at NBH2, PE-based C_{free} was
351 170 ng/L while SPME and SPMD C_{free} values were 110 ng/L and 76 ng/L, respectively. At
352 NBH4, PE-based C_{free} values were 31 ng/L and SPME and SPMD C_{free} values were 18 ng/L and
353 7.7 ng/L, respectively. Statistical analysis of the winter deployment data was more complicated
354 to interpret than the fall deployment. At NBH2, C_{free} for PE was significantly different from all
355 other treatments while C_{free} based on SPME and total water were not different, total water and
356 SPMD C_{free} were also not different, and, finally, SPMD and C_{18} -based C_{free} were not different.
357 The NBH4 C_{free} were not different for PE and total water, SPME and C_{18} -based, and SPMD and
358 C_{18} -based.

359
360 Despite the range of C_{free} values, all of the passive sampler-based concentrations were
361 generally within about a factor of two to three of one another suggesting they were
362 “experiencing” (i.e., exposed to) and measuring similar truly dissolved concentrations of PCBs
363 in the ambient water column of the two stations in New Bedford Harbor during their respective
364 deployments. This finding is encouraging and suggests the samplers will provide comparable
365 C_{free} data for PCBs even though they are deployed and analyzed in different ways using various
366 designs and gear, partition coefficients, and assumption regarding equilibrium status. For
367 example, as discussed above, for the SPME, equilibrium was assumed for the winter deployment
368 while the PE data were adjusted for non-equilibrium conditions based on the PRC concentrations

369 using Equation 5. With the exception of CB206 and CB209, which had less than 10%
370 equilibrium and their C_{free} are not reported, the degree of PE non-equilibration by congener
371 ranged from 20 to 96% resulting in a relatively minor difference in the unadjusted and
372 equilibrium adjusted C_{free} for total PCBs after the 29 day winter deployment (i.e., adjusting for
373 non-equilibrium conditions based on the PRCs increased total PCB C_{free} by only 4% to 8%).

374
375 In general, SPMD data would also be adjusted for non-equilibrium conditions based on
376 PRC recovery. As discussed, the PRCs selected for the SPMD in the winter deployment were
377 CB38 and CB50, two congeners not usually found in the commercial Aroclor mixtures known to
378 contaminate NBH. Unfortunately, following deployments, analysis of the SPMD extracts
379 detected concentrations of both congeners at levels close to (NBH4) or exceeding (NBH2) their
380 original amendment concentrations. These results indicate both CB38 and CB50 were present
381 unexpectedly in the NBH water column or matrix interference with similar molecular weights
382 were present. In either case, the PRC data were not viable and equilibrium of the SPMD data
383 was assumed for calculation of the C_{free} . This demonstrates a weakness in using non-Aroclor
384 PCB congeners as PRCs for target PCBs, especially at very contaminated sites, like Superfund
385 sites, where there may be unexpected sources of rare congeners. For the PE, which used
386 brominated biphenyls as PRCs, there was no evidence of a background presence of these
387 compounds in the NBH water column.

388
389 As noted in the Introduction, the value of conventionally-collected total PCBs water
390 concentrations is debatable because of the artifacts that can plague such samples. However, they
391 do serve as a potentially useful point of comparison to passive sampler inferred C_{free} .
392 Similarities in water concentrations of total PCBs, based on total water extraction or C_{18} solid
393 phase extraction, and passive sampler C_{free} varied by station and deployment. For example, in
394 the fall deployment at NBH4, PE C_{free} and aqueous measurements were similar ranging from 21
395 to 25 ng/L (Figure 1a). Similarly, in the winter deployment at NBH4, PE C_{free} were fairly
396 comparable to water concentrations with passive sampler C_{free} values ranging from 7.7 to 31
397 ng/L and aqueous concentrations ranging from 16 to 30 ng/L (Figure 1b). In contrast, at NBH2
398 in the winter deployment, passive sampler C_{free} values ranged more widely 76 to 170 ng/L while
399 aqueous concentrations were 53 to 97 ng/L. As discussed above, the SPMD data was not

400 adjusted for non-equilibrium and may represent under-estimations of C_{free} (76 ng/L) resulting in
401 the coincidental similarity to the lower trending water concentrations.

402
403 *Palos Verdes Shelf* Concentrations of total PCB C_{free} across this site ranged from 45 to 430 pg/L
404 (Figure 2). Stations closer to shore (PVS1 and PVS2) had the lowest total PCB C_{free} (45 to 86
405 pg/L) at the site. Stations PVS3, PVS4 and PVS5, all in the vicinity of the LACSD outfalls,
406 demonstrated the highest C_{free} with values ranging from 220 to 430 pg/L. In addition to the
407 general distribution of C_{free} in the water column, the data in Figure 2 indicate, as expected, that
408 PCBs are originating from the sediments of the site and diffusing from the interstitial water into
409 the water column over time. For example, at all stations where PE samplers were deployed at
410 multiple depths on the current profilers, except PVS6, total PCB C_{free} were observed to increase
411 when approaching the sediment. A second observation is the spatial distribution of total PCB
412 C_{free} . The dominant oceanic current along this section of the Pacific Ocean coastline is the
413 California Current which follows the California coast 200 to 300 Km off-shore with a depth of
414 300 meters moving in a southeastern direction [31]. However, in the area of the California coast
415 where the Palos Verdes Shelf Superfund site is located (i.e., the Southern California Bight), the
416 Southern California Countercurrent forms the Southern California Eddy deflecting water in a
417 direction counter to the California Current; that is, in a northwestern direction [32]. As a
418 consequence, the concentration of water column PCBs and other contaminants associated with
419 sedimentary sources at the site increase in a northwestern direction from the LACSD outfalls.
420 For example, the C_{free} at stations PVS3 and PVS4 reflect these higher values (250 to 430 pg/L)
421 while stations PVS6 and PVS7 (directly to the southeast of the outfalls) show lower C_{free} (90 to
422 180 pg/L). Using passive sampling, Fernandez et al. [18] observed similar depth and spatial
423 distribution trends for DDTs and PCBs in the water column at the Palos Verdes Shelf site.

424
425 A principal goal of this investigation was to evaluate the deployment of passive samplers
426 in deep water without using elaborate deployment gear. As can be seen in Supplemental Data
427 Figure S2b, for this deployment, PE samplers were simply attached to the current profilers with
428 stainless steel wire. Of the 21 samplers deployed, all were recovered successfully (although
429 three were lost or compromised after recovery) demonstrating the versatility and robustness of
430 the PE and simple deployment system. In another study examining water column concentrations

431 using PE and SPME passive samplers deployed at 11 stations at the PVS Superfund site,
432 Fernandez et al. [18] lost several samplers in the middle and upper water column where the
433 current is the strongest. The losses were attributed to fatigue of the aluminum wire used to
434 secure the samplers to the deployment gear. In the same study, the SPME attached to the gear by
435 stainless steel hose clamps were successfully recovered [18] as were SPME samplers Zeng et al.
436 [33] deployed, also using stainless steel hose clamps, in another study in the Southern California
437 Bight.

438
439 *Naval Station Newport* Baseline C_{free} was determined for three categories of target contaminants
440 of regulatory concern including high molecular weight (MW) PAHs, B[a]P and total PCBs
441 (Figure 3), Additionally, total PAHs and total PBDEs were investigated (Supplemental Data
442 Figure S3). High MW PAHs C_{free} ranged from 8.9 to 16 ng/L and 3.2 to 6.0 ng/L based on PE
443 and POM, respectively, demonstrating an approximate factor of two difference in C_{free} between
444 polymers. Using PE, B[a]P, a component of the high MW PAHs, C_{free} values ranged from 100
445 to 780 pg/L compared to POM-based C_{free} values which ranged from 100 to 220 pg/L. The
446 B[a]P C_{free} values showed at most a factor of three difference between polymers (e.g., NSN2).
447 Total PCB C_{free} ranged from 110 to 170 pg/L based on PE while C_{free} using POM were much
448 lower, ranging across the site from 5.8 to 11 pg/L. Total PCB C_{free} were the lowest at this
449 Superfund site as compared to the other two Superfund sites in this investigation. Total PAH
450 and PBDE C_{free} ranged from 25 to 48 ng/L and 130 to 230 pg/L, respectively, for the PE-based
451 measures. These values are very similar to the POM-based measures of C_{free} across the site: 16
452 to 40 ng/L for total PAHs and 160 to 170 pg/L for total PBDEs (Supplemental Data Figure S3).
453 Differences in total PCB C_{free} between the PE- and POM-based estimates are the largest we
454 found across this entire investigation. Analysis of POM for PCB congeners found much lower
455 accumulation than in the PE: POM C_{free} were, on average, only 6% of PE C_{free} . In addition,
456 POM accumulated a smaller diversity of PAH molecules compared to PE. Further, PRC data for
457 the POM was problematic when used for adjusting any of the target contaminants for non-
458 equilibrium conditions. Consequently, for POM, C_{free} was calculated using Equation 2 which
459 assumes the target contaminants have attained equilibrium with the polymer. In this case, it is
460 uncertain if that assumption is accurate. It is unclear what caused the problems when working
461 with POM and PRCs in this investigation but the loss of PRCs from the polymer was not found

462 to be linearly correlated with contaminant molecular weight or K_{OW} . In a previous deployment,
463 Perron et al. [19] also reported difficulties working with PRCs and POM when trying to calculate
464 C_{free} for PCBs. In general, as shown in New Bedford Harbor, C_{free} based on different samplers
465 were relatively similar lending weight to the conclusion that the samplers “experienced” and
466 measured similar C_{free} in the water column. Supplemental Data Table S1 shows the results of
467 statistical analyses comparing C_{free} by passive sampler type and station. Specific trends from the
468 analysis include total PCB C_{free} values, as well as high molecular weight PAH C_{free} values, based
469 on PE and POM were always statistically different. Further, PE- and POM-based total PAHs
470 C_{free} values were never significantly different. In between these extremes, significant differences
471 in PE and POM C_{free} values occurred at 50% of the stations for B[a]P and total PBDEs

472

473 *Passive Sampler Equilibrium at the New Bedford Harbor Superfund Site*

474 Deployments performed at the New Bedford Harbor Superfund site offer a unique
475 opportunity to assess passive sampler equilibrium status. This is because several different types
476 of samplers were deployed over multiple time periods. As discussed above, for the SPMDs and
477 SPMEs equilibrium was assumed while for PE, PRCs were used to adjust C_{free} for non-
478 equilibrium conditions. It should be noted that for the SPMDs, because of the polymers
479 thickness on two sides (i.e., tube configuration), this assumption is suspect and the reported
480 concentrations may represent underestimates. Beyond assuming equilibrium or using PRCs,
481 other empirical approaches for assessing the equilibrium status of the passive sampler can be
482 used. One is to perform a temporal series analysis, collecting passive samplers over time to
483 assess when target contaminant concentrations no longer show statistically significant changes in
484 the passive sampler polymer. As discussed above, a time series analysis was performed with
485 PE, SPME and SPMD in the winter deployments at New Bedford Harbor. Figure 4 shows the
486 concentrations of total PCBs over the 29 day deployment at seven day intervals for each sampler.
487 In general, all three samplers showed similar trajectories for total PCB uptake. For example, by
488 Day 29, concentrations of total PCBs ranged from 29,000 to 39,000 ng/mL polymer and 3,200 to
489 7,500 ng/mL polymer at stations NBH2 and NBH4, respectively. Statistical analysis indicated
490 the SPMD samplers were continuing to accumulate PCBs at NBH2 after 21 days but had
491 achieved equilibrium after Day 21 at NBH4 (i.e., no statistically significant difference between
492 polymer and triolein concentrations on days 21 and 29) (Figure 4a). In contrast, after 14 days at

493 NBH2, the SPME samplers were at equilibrium while at NBH4 days 21 and 29 were
494 significantly different and equilibration had not been achieved (Figure 4b). Finally, analysis of
495 the winter PE samplers suggests equilibrium was achieved after 14 and 21 days at NBH2 and
496 NBH4, respectively (Figure 4c). This finding agrees with the relatively small PRC-based
497 correction (< 10%) applied to the winter PE to adjust for non-equilibrium conditions discussed
498 above. A similar analysis is provided in the Supplemental Data section for selected PCB
499 congeners (Supplemental Data Figures S4, S5).

500

501 For a seasonal comparison, Figure 4d shows the accumulation of total PCBs by the PE in
502 the fall deployment indicating equilibrium by days 21 and 14 at NBH2 and NBH4, respectively.
503 At NBH4, the final deployment period (day 28) was similar to the final concentration in the
504 winter deployment (day 29): 7,700 ng/mL PE versus 7,500 ng/mL PE. However, at NBH2 and
505 unlike NBH4, concentrations of total PCBs were much higher in the fall relative to the winter
506 deployment: 84,000 ng/mL PE versus 39,000 ng/mL PE. Interestingly, the total water and C₁₈-
507 based measures of total PCBs indicated that during the fall deployment, NBH2 and NBH4
508 concentrations were often also elevated compared to the winter deployment (Figure 5a, b).

509

510 One other approach for assessing equilibrium status, is to measure the concentration of
511 target contaminants in polymers of different thicknesses. The premise for this approach is that as
512 target contaminants accumulate they will partition homogeneously within the polymer.
513 Therefore, when expressed on a mass or volume basis, for two different polymer thicknesses,
514 equal concentrations would indicate equilibrium. This type of analysis was performed with two
515 PE thicknesses (i.e., 25 μm and 51 μm) in both fall and winter deployments at NBH2 and NBH4.
516 At both stations, in the winter, after 29 days there were no statistical differences between
517 thicknesses, suggesting the PE was at equilibrium (Figure 6a, b). Conversely, at both NBH2 and
518 NBH4, in the fall, after 28 days, the two thicknesses were statistically different suggesting
519 equilibrium had not yet been achieved (Figure 6a, b). As noted previously, relatively higher total
520 water concentrations of PCBs in the fall deployment were observed during some of the
521 collections (Figure 5).

522

523 *Comparing Passive Sampler Uptake and Mussel Bioaccumulation*

524 Thus far, the focus of this study has been on examining contaminant C_{free} (i.e., PCBs,
525 PAHs, PBDEs) in the water column at three Superfund sites and assessing equilibrium based on
526 the concentration of PCBs in the polymer at the New Bedford Harbor Superfund site. However,
527 another very valuable type of information that passive samplers can provide is an estimate of
528 concentrations of target contaminants that organisms are likely to bioaccumulate. Currently,
529 biomonitoring organisms, like marine polychaetes and mussels, and freshwater and marine fish,
530 are used to determine the amount of bioavailable contaminants in the water column and
531 interstitial waters of Superfund sites [34]. This information has been used for several purposes
532 including assessing the effectiveness of remediation and performance of long-term monitoring
533 [34, 35]. However, there are limitations to using organisms for measuring bioavailable
534 concentrations. These include field conditions (e.g., high or low water temperatures, low
535 dissolved oxygen, ice formation) adversely affecting biomonitoring organisms, seasonal
536 unavailability of biomonitoring organisms, and logistical challenges and financial costs
537 associated with deploying living organisms [36]. The concept of using passive samplers as
538 surrogates for biomonitoring organisms when such limitations are an issue has a great deal of
539 appeal. Scientific data comparing biomonitoring organisms and passive samplers continues to be
540 collected in order to evaluate this approach [12, 16, 23-25, 37]. In the current study, mussels
541 were deployed during the fall passive sampler deployment at New Bedford Harbor and provide
542 an opportunity to compare mussel bioaccumulation with passive sampler accumulation of PCBs
543 at two stations.

544
545 Mean concentrations of total PCBs in deployed mussels at NBH2 and NBH4 were
546 350,000 ng/g lipid and 64,000 ng/g lipid, respectively. By comparison, total PCB PE
547 concentrations adjusted for non-equilibrium conditions were 110,000 ng/g PE and 9,300 ng/g PE
548 for samplers at NBH2 and NBH4, respectively. This difference results in a mussel
549 bioaccumulation to PE accumulation ratio of 3.2 and 6.9 for NBH2 and NBH4, respectively.
550 Hofelt and Shea [37], in their study in NBH, reported total PCB ratios for mussel
551 bioaccumulation to SPMD accumulation ranging from about 1.2 to 4.8. Based on Equation 7,
552 these tissue concentrations expressed, on a mussel lipid basis, are equivalent to mussel-based
553 C_{free} of 404,000 pg/L and 58,000 pg/L at NBH2 and NBH4, respectively. These values compare
554 relatively well to polyethylene-based C_{free} of 360,000 pg/L and 25,000 pg/L at NBH2 and NBH4,

555 respectively. However, to more directly compare mussel bioaccumulation to passive sampler
556 accumulation, Figure 7 shows mussel and PE concentrations of individual PCB congeners at
557 NBH2 and NBH4. There were a total of 27 congeners that had matching accumulation data for
558 both mussels and PE. If mussels and polyethylene accumulated PCB molecules identically, the
559 data points in Figure 7 would fall on the 1:1 line. Instead, a mean offset of approximately 8.6 is
560 observed indicating, that in general, the mussels accumulated PCBs about nine times more than
561 the PE. In addition, the offset suggests a concentration dependency on the amount of PCB
562 congeners in the overlying water. In other words, at NBH4, where C_{free} is relatively low (Figure
563 1a), the offset ranges from a factor of 2.9 to 22 and at NBH2, where C_{free} is relatively high
564 (Figure 1b), the offset range is a factor of 1.5 to 15. Despite the offset, summary statistics
565 demonstrate a strong correlative log-linear relationship between mussel bioaccumulation and PE
566 accumulation:

567

$$\text{Log PCB bioaccumulation (ng/g lipid)} = 0.74 * \text{Log PCB accumulation (ng/g PE)} + 1.62$$

568

$$(r^2 = 0.92; n = 27; p \lll 0.05)$$

569

570

571 Further, the log-linear correlation indicates the relationship between bioaccumulation and PE
572 accumulation is highly significant with p values much less than 0.05 (Figure 7). In a similar
573 comparison of PCB passive sampler accumulation versus bioaccumulation, using the marine
574 polychaete *Nereis virens* exposed to New Bedford Harbor sediment, Friedman et al. [24] also
575 reported a strong linear relationship ($r^2 = 0.88$; $n = 48$). In addition, Gschwend et al. [16], using
576 PCB-contaminated sediments from the Hunter's Point Naval Station in San Francisco Bay (CA,
577 USA), exposed to the marine polychaete *Neanthes arenaceodentata*, under two exposure regimes
578 (i.e., mixed and passive), reported linear relationships: $r^2 = 0.64$ ($n = 7$) and $r^2 = 0.59$ ($n = 7$),
579 respectively. Interestingly, in the Gschwend et al. [16] comparison of polychaete
580 bioaccumulation to passive sampler accumulation, they also included PDMS-coated SPME
581 fibers and POM. In all four cases, they found an off-set between the 1:1 line between
582 bioaccumulation and accumulation similar in behavior (i.e., linear and favoring bioaccumulation)
583 and scale (i.e., an order of magnitude) to the one described in the current study. They attributed
584 the off-set to the preferential partitioning of PCBs to lipid as compared to the polymers.

585 This representative selection of measures demonstrates that PE accumulation is correlated
586 and potentially predictive of organism bioaccumulation, which in turn, suggests PE could be
587 considered as a surrogate for biomonitoring organisms (at least at the New Bedford Harbor
588 Superfund site with PCBs). In their evaluation of the relationship between SPMD accumulation
589 and bioaccumulation from a review of nine studies (including Hofelt and Shea [37]), Booij et al.
590 [38] recommended using passive sampling (in this case SPMDs) for new biomonitoring
591 programs because of the associated advantages relative to the disadvantages of using
592 biomonitoring organisms. These advantages include: $K_{\text{lipid-free}}$ show greater variability than $K_{\text{PS-}}$
593 free ; determining equilibrium status is more difficult with organisms compared to passive
594 samplers; and the need to use different organisms (to accommodate different habitats) limits the
595 standardization of methods across broad geographic areas, whereas one type of passive sampler
596 can be applied everywhere. For existing monitoring studies, Booij et al. [38] acknowledged that
597 switching from biomonitoring organisms to passive samplers is problematic because of the
598 potential loss in data consistency. However, they suggest the performance of multiple
599 comparative studies on a site-specific basis to develop conversion factors between historic
600 bioaccumulation and new passive sampler accumulation data. Similarly, the concept of the
601 systematic global deployment of aquatic passive samplers for monitoring purposes has recently
602 been proposed in the literature [39, 40]. Despite the off-set observed in this dataset and others
603 (e.g., [16]), there is growing evidence that passive sampler accumulation of PCBs is linearly
604 correlated with organismal bioaccumulation suggesting these are predictive relationships that
605 could be useful in instances when the deployment of biomonitoring organisms is not viable.
606

607 *Comparison of Passive Sampler-based C_{free} to Other Studies*

608 Of the three Superfund sites investigated, New Bedford Harbor has been the most
609 frequently studied using passive samplers. For example, several studies have used passive
610 samplers to examine the distribution and bioavailability of contaminants in NBH sediments.
611 Specifically, Vinturella et al. [23], Friedman et al. [24] and Lu et al. [25] evaluated PE and
612 SPME as surrogates for measuring the bioaccumulation of PCBs and PAHs by a benthic
613 polychaete (*Neries virens*) and an oligochaete (*Ilyodrilus templetoni*). Other than the current
614 study, only Hofelt and Shea [37] have used passive sampling to estimate the C_{free} of PCBs in the
615 New Bedford Harbor water column. They performed 30 day SPMD deployments at five stations

616 inside and outside of the harbor and detected several organochlorine pesticides and PCBs. Total
617 PCB C_{free} based on SPMDs ranged from 1,400 to 17,000 pg/L (Table 2). By comparison, total
618 PCB C_{free} in the current study was about an order of magnitude greater: 25,000 to 359,000 pg/L
619 based on PE; 18,000 to 107,000 pg/L based on SPME; 8,000 to 76,000 pg/L based on SPMD.
620 While the studies were performed about ten years apart they analyzed for the same PCB
621 congeners to determine total PCBs. Consequently, it is not clear why such large differences in
622 total PCB C_{free} exist between the investigations.

623
624 Three previous studies used passive sampling to investigate the C_{free} of total PCBs and
625 DDTs at the Palos Verdes Shelf Superfund site. Zeng et al. [33] applied SPME to estimate the
626 C_{free} of total DDTs two meters above the sediment surface in 30 day deployments resulting in
627 4,900 pg/L at a station close to the current investigation's stations (Table 2). In one of two
628 studies at PVS, Fernandez et al. [18] deployed PE and SPME samplers at three depths in the
629 water column at 11 stations. For samplers five meters above the sediment, C_{free} for total DDTs
630 ranged from 260 to 1,100 pg/L using SPME and 750 to 2,600 pg/L for PE. The differences in
631 the heights of the samplers above the sediments (5 m versus 2 m) may explain the lower C_{free}
632 values in the present study when compared to Zeng et al. [33] measurements. For total PCBs at
633 PVS, the current study found C_{free} ranged from 45 to 430 pg/L while Fernandez et al. [18]
634 reported 90 to 320 pg/L for PE samplers deployed 5 meters above the sediment surface. In a
635 second study, Fernandez et al. [19] measured C_{free} of 230 to 460 pg/L and 130 to 450 pg/L with
636 PE and POM, respectively, located about 20 cm above the sediment surface. For total PCBs, all
637 of these C_{free} values from the different studies are relatively similar despite using different types
638 of passive samplers over a ten year period of time; for example, high C_{free} values ranged from
639 320 to 460 pg/L. Further, any substantial differences can be explained by the depth the samplers
640 were deployed (i.e., higher in the water column resulted in lower target contaminant
641 concentrations) indicating the sediments serve as the primary source of target contaminants at
642 PVS. In addition, Fernandez et al. [19] found total DDT C_{free} in the water column ranging from
643 26,000 to 32,000 pg/L and 7,800 to 16,000 pg/L using PE and POM, respectively, in samplers
644 deployed about 20 cm above the sediment surface. In the same study, SPME deployed
645 approximately one meter above the sediments measured C_{free} of 1,700 to 4,000 pg/L. Finally, in
646 both Fernandez et al. [18, 19], SPME were deployed to monitor for total PCB C_{free} but unlike the

647 total DDTs, no PCBs were detected analytically. In contrast, both PE and POM were able to
648 detect total PCB C_{free} in the water column at PVS. This difference in the sampler's performance
649 most likely reflects the greater mass of PE and POM that can be deployed compared to SPME.
650 While SPME achieves equilibrium more rapidly than POM or PE, the smaller mass of PDMS
651 that is generally deployed is sometimes unable to accumulate sufficient target contaminant for
652 detection by analytical instrumentation. However, other configurations of PDMS can be
653 deployed [e.g., 41] and attain greater detection sensitivity than afforded by SPME.

654
655 Finally, no previous studies using passive samplers have investigated C_{free} in the water
656 column at the Naval Station Newport Superfund site. However, Perron et al. [20, 21] reported
657 C_{free} total PCBs, total PAHs and total PBDEs of 38 to 120 pg/L, 32 to 91 ng/L and 40 to 91 pg/L,
658 respectively, using PE and POM passive samplers for a station in Newport Harbor about 5.5
659 kilometer south of the Superfund site (Table 2). In general, these concentrations compare
660 relatively well with C_{free} reported in the present study where total PCBs, total PAHs and total
661 PBDEs based on PE were 110 to 170 pg/L, 26 to 40 ng/L and 160 to 230 pg/L, respectively, and
662 based on POM were 5.8 to 11 pg/L, 16 to 40 ng/L and 160 to 170 pg/L, respectively. The
663 decades of industrial maritime activity and the resulting sediment contamination at NSN make
664 the higher total PCB C_{free} there compared to Newport Harbor unsurprising. Further, Newport
665 Harbor is an active commercial and recreation harbor, therefore elevated total PAH C_{free} from
666 boat engines and related sources is not unexpected. However, what is of interest are the elevated
667 C_{free} for total PBDEs at NSN. These chemicals are used as flame retardants in some consumer
668 products and are undergoing scrutiny in the United States and Europe because of concerns with
669 mammalian toxicity. The levels at NSN were up to three times higher than those seen in
670 Newport Harbor (and anywhere else in Narragansett Bay [21]) suggesting there may be an
671 unknown source in the NSN that requires further investigation.

672 673 **Summary**

674 In general, the different passive samplers demonstrated good agreement in C_{free} with
675 values varying by a factor of two to three. This level of agreement was clearly demonstrated at
676 the Palos Verdes Superfund site where C_{free} determined by different passive samplers over
677 several years and deployments varied by less than a factor of two. Further, in most instances

678 where conventional water samples were collected (i.e., grabs) and compared to passive sampler
679 C_{free} values (i.e., New Bedford Harbor), values were also within a factor of two of aqueous
680 measurements. Also, in most cases in New Bedford Harbor, total PCBs were approaching
681 equilibrium in the samplers after nearly 30 days of deployment. These findings suggest all of the
682 samplers were experiencing and measuring the same C_{free} during their respective deployments
683 and that the RPM's selection of which passive samplers to use at their site can be based on
684 variable like costs, availability and logistics rather than which passive sampler is more
685 scientifically accurate. More importantly, passive sampling will enable the RPM to determine
686 both the spatial and temporal trends of target contaminants, key factors for successfully
687 remediating a contaminated site. At New Bedford Harbor, a strong log-linear, correlative and
688 predictive relationship was found between passive sampler accumulation and mussel
689 bioaccumulation. Finally, all of the Superfund site investigations discussed here, except for the
690 SPMD deployments, used unsophisticated deployment gear and passive samplers. This
691 evaluation demonstrates the practical utility of passive sampling for generating scientifically
692 accurate water column C_{free} which is critical for making informed environmental management
693 decisions at contaminated sediment sites.

694

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890 **Table Legends**

891 Table 1. Superfund sites, sampling stations deployment locations, water depths, and sample types
892 (e.g., polyethylene (PE), solid phase microextraction (SPME), polyoxymethylene (POM), semi-
893 permeable membrane devices SPMDs).

894
895 Table 2. Comparison of C_{free} concentrations for several organic contaminants in the water
896 column of the Superfund sites investigated in this study. Available C_{free} ranges observed in other
897 studies using passive sampling are also presented.

898
899 **Figure Legends**

900
901 Figure 1. Total PCB C_{free} measured in the water column of the New Bedford Harbor Superfund
902 site (New Bedford, MA, USA) during (a) the fall deployments of polyethylene (PE), mussels,
903 and collection of total and C_{18} -based grab water samples and (b) the winter deployments of
904 polyethylene (PE), solid phase microextraction (SPME), semi-permeable membrane devices
905 (SPMDs), and collection of total and C_{18} -based grab water samples. Total PCB is equivalent to
906 the sum of measured PCB congeners.

907
908 Figure 2. Total PCB C_{free} measured in the water column of the Palos Verdes Shelf Superfund site
909 (CA, USA) during polyethylene (PE) deployments. Total PCB is equivalent to the sum of
910 measured PCB congeners.

911
912 Figure 3. High molecular weight PAH (a), benzo[a]pyrene (b), and total PCB (c) C_{free} measured
913 in the water column of the Naval Station Newport Superfund site (Newport, RI, USA) during the
914 polyethylene (PE) and polyoxymethylene (POM) deployments. High molecular weight PAH was
915 equivalent to the sum of pyrene, fluoranthene, chrysene, benzo[a]pyrene, benz[a]anthracene and
916 dibenz[a,h]anthracene. Total PCB is equivalent to the sum of measured PCB congeners. Note:
917 concentrations of benzo[a]pyrene and total PCBs are in pg/L and high molecular weight PAH
918 concentrations are in ng/L.

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920 Figure 4. Total PCBs accumulated by (a) SPMD, (b) SPME, and (c) PE during the winter
921 deployment, and (d) PE during the fall deployment over multiple sampling periods at the New
922 Bedford Harbor Superfund site. Statistically significant differences ($\alpha = 0.05$) between sampler
923 concentrations for the last deployment period (day 28 or 29) and previous deployment periods
924 are indicated by *. Total PCB is equivalent to the sum of measured PCB congeners.

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926 Figure 5. Total PCBs based on total water and C₁₈-based measurements during fall and winter
927 sampling periods at stations (a) NBH2 and (b) NBH4 of the New Bedford Harbor Superfund site.
928 Total PCB is equivalent to the sum of measured PCB congeners.

929
930 Figure 6. Total PCBs in polyethylene (PE) passive samplers of different thicknesses (e.g., 25 μm
931 and 51 μm) at (a) NBH2 and (b) NBH4 in the fall and winter deployments. Significant statistical
932 differences ($\alpha = 0.05$) between thicknesses at a given station and season are indicated by *. Total
933 PCB is equivalent to the sum of measured PCB congeners.

934
935 Figure 7. Concentration of PCB congeners accumulated by polyethylene (PE) passive samplers
936 versus bioaccumulated by blue mussels (*Mytilus edulis*) during the fall deployment at the New
937 Bedford Harbor Superfund site. Open and full circles represent stations NBH2 and NBH4,
938 respectively. Polyethylene concentrations have been adjusted for equilibrium conditions.