Improvements in pollutant monitoring: Optimizing silicone for co-deployment with polyethylene passive sampling devices

IMPROVEMENTS IN POLLUTANT MONITORING: OPTIMIZING SILICONE FOR

CO-DEPLOYMENT WITH POLYETHYLENE PASSIVE SAMPLING DEVICES

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ABSTRACT

Sequestering semi-polar compounds can be difficult with low-density polyethylene (LDPE), but those pollutants may be more efficiently absorbed using silicone. In this work, optimized methods for cleaning, infusing reference standards, and polymer extraction are reported along with field comparisons of several silicone materials for polycyclic aromatic hydrocarbons (PAHs) and pesticides. In a final field demonstration, the most optimal silicone material is coupled with LDPE in a large-scale study to examine PAHs in addition to oxygenated-PAHs (OPAHs) at a Superfund site. OPAHs exemplify a sensitive range of chemical properties to compare polymers (log K_{ow} 0.2-5.3), and transformation products of commonly studied parent PAHs. On average, while polymer concentrations differed nearly 7-fold, water-calculated values were more similar (about 3.5-fold or less) for both PAHs (17) and OPAHs (7). Individual water concentrations of OPAHs differed dramatically between silicone and LDPE, highlighting the advantages of choosing appropriate polymers and optimized methods for pollutant monitoring.

KEYWORDS

Polyethylene; silicone; passive sampling; PAHs; OPAHs; oxygenated-PAHs; pesticides

CAPSULE

Silicone passive sampling is optimized through laboratory methods, and OPAHs highlight differences between polyethylene and silicone passive samplers in aqueous field deployments.

HIGHLIGHTS

49   •   Silicone passive sampler membranes are best cleaned with a combination of non-polar

50   and semi-polar solvents

51   •   Silicone membranes sequester pesticides and other pollutants more consistently with

52   lower log K_{ow} values than LDPE

53   •   PAHs and OPAHs are present in similar concentrations at a Superfund site

54   •   More individual OPAHs are consistently sequestered with silicone than with LDPE

55   passive samplers

56

57

INTRODUCTION

Many benefits of passive sampling are practical, whether it is cost, ease of use over grab samples, concentrated extracts over diffuse matrices, or time-weighted averages over the deployment period (Namieśnik et al., 2005; Vrana et al., 2005; Zabiegala et al., 2010; Seethapathy and Gorecki, 2012). Another important benefit is that passive sampling concentrations represent bioavailable contaminants in the sample media (Anderson and Hillwalker, 2008). One challenge with passive sampling is choosing a receiving phase among the many diverse options that exist. For example, at least 22 different types of materials, sorbents, or solvents are reported as receiving phases for passive sampling in a recent review (Vrana et al., 2005). Some PSDs specialize in targeting polar or non-polar compounds, and some materials can be used in tandem with others to broaden the total range of sequestered compounds (Petty et al., 2004; Harman et al., 2012; Allan et al., 2013). In addition to compound selectivity, considerations for using PSDs derive from previous development of uptake kinetics and published laboratory methods (Vrana et al., 2005; Rusina et al., 2007). One of the most commonly used passive samplers is low-density polyethylene (LDPE) due to the low cost of the material, hydrophobic properties for targeting many persistent organic pollutants (POPs), and available partitioning and sampling rate estimates (Booij et al., 2002; Anderson et al., 2008; Choi et al., 2013).

However, LDPE does not sequester lower log K_{ow} compounds (especially below 4) as well as another polymer, silicone (Rusina et al., 2007; Allan et al., 2013). Silicone has become an increasingly popular passive sampler in the past 10 years, and has been compared with LDPE to see differences in sequestration of target chemicals (Allan et al., 2010; Allan et al., 2013).

81 Although quantitative comparisons between aqueous concentrations were similar (< 2 to 3-fold

82 among PAHs and PCBs), a dramatic increase of absorbed analytes was seen using silicone over

83 LDPE for compounds with log K_{ow} values lower than 6 (Allan et al., 2013). More efficient

84 absorption of analytes into the polymer can result in several advantages, including greater

85 flexibility in deployment times, lower detection limits, and applications to bioassays due to

86 greater concentrations in samples as long as extracts or silicone polymer background may be

87 sufficiently reduced. Explaining sequestration differences between LDPE and silicone begin

88 with the structural make-up of each polymer. Silicone is made of a silicon-oxygen backbone

89 with various functional groups bonded to silicon such as methyl, phenyl, vinyl, or fluoro

90 constituents (Rusina et al., 2007; Seethapathy and Gorecki, 2012). In contrast, LDPE consists of

91 carbon and hydrogen (Rusina et al., 2007), which gives this polymer a more hydrophobic

92 property. Differences in chemical structures of polymers influence intermolecular forces acting

93 between the target compounds and the polymers in the sampled media. Along with compound

94 diffusivity, the resulting fugacity of compounds out of the aqueous phase into the polymers can

95 be modeled using first order kinetics.Ultimately, both polymers yield more accurate data than

96 other passive sampling devices (Allan et al., 2010), so advantages of using one or the other

97 depend on the choice of targeted compounds. Unlike previous comparisons of silicone and

98 LDPE which focused on POPs (Allan et al., 2010; Allan et al., 2013), this research includes

99 compounds that are transformation products of pollutants.   One class of compounds that is well

100 suited for a comparison between silicone and LDPE is oxygenated-PAHs (OPAHs). OPAHs are

101 degradation products of PAHs (Lundstedt et al., 2007), and are emerging contaminants of

102 interest that have log K_{ow} values less than 6 for 22 previously studied OPAHs (O'Connell et al.,

103 2013). Other classes of pollutants, such as pesticides, span a wide range of chemical properties

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104 that are also beneficial for polymer comparisons. By addressing data gaps through monitoring

105 emerging compounds of interest using passive samplers, this research can highlight differences

106 in silicone and LDPE and ultimately assess a greater range of contamination. Considering the

107 chemical structure of the silicone polymer and previous evidence illustrating polymer differences

108 in sequestration, silicone should sequester higher concentrations and a greater range of OPAH

109 compounds than LDPE.

110

111 Therefore, our objective focused on three aims. First, laboratory methods were employed to

112 optimize silicone pre-deployment cleaning to reduce background chromatographic interferences,

113 and for infusing silicone with labeled internal standards for uptake rates and water concentration

114 estimates. Second, we compared five silicone polymers in a field application at a Portland

115 Harbor Superfund site with a history of POP (including PAH and pesticide) contamination

116 (Sethajintanin and Anderson, 2006; Sower and Anderson, 2008). Sequestration data and

117 operational logistics were used to select silicone polymers best suited for co-deployment studies

118 with LDPE.   Finally, the optimal silicone was compared with LDPE for PAHs and OPAHs. By

119 optimizing silicone passive samplers to be used in tandem with LDPE, this work provides a field

120 validated method for quantification of a wide range of contaminants including PAHs, OPAHs,

121 and pesticides.

122

123 **METHODS**

124 *Analyte information*

125 OPAH, PAH, and single pesticide standards were bought from Sigma Aldrich (St. Louis, MO),

126 Chiron (Trondheim, Norway), and Fluka (part of Sigma-Aldrich). Pesticide and PAH mixes

127 were purchased from Accustandard (New Haven, CT).   Labeled standards used as performance

128 reference compounds (PRCs), laboratory surrogates, or instrument internal standards were

129 obtained from either CDN Isotopes (Pointe-Claire, Quebec, Canada), or Cambridge Isotope

130 Laboratories (Tewksbury, MA). A complete list of all quantitative analytes including surrogates,

131 PRCs, and internal standards is given in the Supporting Information (**Table S1**). All solvents

132 were Optima-grade or equivalent (Fisher Scientific, Pittsburgh, PA), and all laboratory water

133 used for infusions or post-deployment cleaning was filtered through a Barnstead D7389 purifier

134 (Dubuque, IA).

135

136 *Polymer construction*

137 A total of five silicone polymers were purchased from three companies: Stockwell Elastomerics

138 Inc. (Philadelphia, PA), Altec Products Limited (Bude, Cornwall, UK), and CS Hyde Company

139 (Lake Villa, IL) (**Table 1**). Silicone was purchased in square-yard rolls, and strips were cut from

140 the sheet using a table cutter/trimmer (Fletcher-Terry Company, Farmington, CT). The AteSil™

141 silicone was purchased as talc-free silicone in 30 x 30 cm sheets. Three AteSil™ strips were cut

142 and extracted together to obtain approximate dimensions of the other polymer strips. All

143 deployed strips were of similar dimensions, approximately 91 cm x 2.6 cm, although thickness

144 differed between materials (**Table 1**). Random subsets of strips were weighed during

145 construction to determine variability, and averages were used to normalize absorption data

146 (**Table 1**). Polyethylene strips were cut from pre-sized layflat tubing (width approximately 2.7

147 cm) at 110 cm, and loops were formed on each end for deployment after heat-sealing each end.

148 Total length of LDPE strips were approximately 100 cm.

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Table 1. Silicone and LDPE polymers by manufacturer, abbreviation, and physical information

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Supplier	PSD Material (Abbreviation)	Depiction	Strip Surface Areas (cm^2)	Strip Volume (cm^3)	Strip Weight (n = 5, g)
Stockwell Elastomerics	Silicone Sponge (**SS**)		~480	~18	15.5 ± 1.4
Stockwell Elastomerics	Thin Translucent Sheet (**ST**)		~480	~7.2	7.87 ± 0.34
CS Hyde	Commercial-Grade Sponge (**CS**)		~480	~18	17.6 ± 0.10
CS Hyde	Translucent Sheet (**CT**)		~480	~18	27.9 ± 0.26
Altec Products Limited	AlteSil™ (**AA**)		~470	~11	15.4 ± 0.33
Brentwood Plastic, Inc.	Low density polyethylene (**LDPE**)		~540	~5.1	4.82 ± 0.08

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Laboratory optimization: pre-cleaning, infusion, post-deployment cleaning, and extraction

Before deployment, silicone was cleaned with solvents to remove chromatographic interferences

from the curing process of the polymer (Rusina et al., 2007). Initially, silicone extraction and

pre-cleaning experiments used ethyl acetate since it does not severely impact the integrity of the

silicone itself (Rusina et al., 2007), and ethyl acetate is a solvent with both polar and non-polar

properties that might be conducive to OPAHs. In addition, to exploit inherent differences in

164 each polymer, ethyl acetate was used as the primary solvent for silicone, while the more non-

165 polar hexane was used for LDPE cleaning as previously described (Anderson et al., 2008). Pre-

166 cleaning experiments for silicones were adapted from several studies (Booij et al., 2002; Rusina

167 et al., 2007; Yates et al., 2007; Allan et al., 2009; Schafer et al., 2010). Ultimately, sufficient

168 reduction of siloxane background was only achieved with a combination of three extraction

169 periods of 1:1, hexane:ethyl acetate, followed by two more periods of 1:1 methanol:ethyl

170 acetate. Roughly 65 g of silicone was placed into an amber jar (1L) before the mixed solvents

171 were added to fill each container. Each extraction period was at least 2 hours, but no more than

172 14 hours (overnight). Samples were shaken at approximately 60 rotations per minute (rpm) in a

173 water bath at 40 °C (New Brunswick Scientific, Edison, NJ). Once an adequate pre-cleaning

174 method was finalized, a secondary experiment evaluated the effectiveness of using recycled

175 solvents to reduce waste. Silicone strips were cleaned with a portion of solvents re-used from a

176 previous exchange (see **Figure S1** for more details). All polymers were dried under filtered

177 vacuum in either sealed glassware or stainless steel kegs (AEB Kegs, Delebio SO, Italy).

178

179 Deployed polymers for the final comparison were spiked with non-target deuterated compounds,

180 (also known as performance reference compounds, or PRCs) used to estimate *in-situ* sampling

181 rates in order to calculate water concentrations (Booij et al., 1998; Booij et al., 2002; Huckins et

182 al., 2002). Infusion solutions were modified to a 50% mixture of methanol/water rather than

183 80% used in a previous study (Booij et al., 2002). Increasing the water content increases the

184 fugacity of the PRC compounds into the silicone, and reduces the total amount of compound

185 needed for the infusion process. Briefly, 5-6 strips (or 60-90 g of silicone) were placed into a 1

186 L amber glass jar and filled with 750 mL of methanol/water (1:1, v:v). PRC compounds were

187   spiked into the solution and allowed to equilibrate with the silicone for 3 days at 60 rpm and

188   40°C. Fluorene-d10, benzo[b]fluorenthene-d12, p,p-DDE-d4, and 9,10-anthraquinone-d8 were

189   used for both silicone and LDPE, and spiking concentrations were adjusted for differences in

190   partitioning, polymer mass, and length of deployment (Booij et al., 2002). Polyethylene was

191   infused with PRCs at 4 to 100 µg per strip directly spiked within the tubing before sealing the

192   other end of the strip.

193

194   After deployment, each polymer was cleaned with ambient waters to remove any surface

195   sediment or biological material on the polymer (**Figure 1**). Once in the laboratory, silicone was

196   rinsed further with filtered water and isopropanol, while LDPE was rinsed with water, dilute

197   hydrochloric acid, and isopropanol based on previous work (Allan et al., 2012). Post

198   deployment-cleaned strips were stored at -20 °C until extraction. Laboratory surrogates (**Table

199   S1**) were spiked into amber jars at 500 ng/mL before extraction. Individual silicone strips were

200   extracted with two sequential rounds of 100 mL of ethyl acetate on an orbital shaker set at 60

201   rpm (ambient temperature), and the total extraction time was 18 hours. LDPE was extracted

202   with hexanes in a similar fashion (Anderson et al., 2008). All extracts were quantitatively

203   concentrated to 1 mL using closed cell evaporators (TurboVaps®, Biotage, Charlotte, NC), and

204   transferred to chromatography vials. Extracts were stored at 4 °C until analysis.

205

206   *Site characterization*

207   Portland Harbor Superfund is located in downtown Portland, OR, and stretches approximately

208   nine miles along the Willamette River. Contaminants of concern at this site include PCBs,

209   dioxins, PAHs, pesticides, and heavy metals (USEPA, 2013). Site names in this study use rough

210 river mile (RM) designations and are not strict distances, but the latitude and longitude of each

211 study site can be found in **SI-Table 2**. In 2010, five silicone polymers were deployed at RM 3.5

212 west (W), while in 2011, just three silicones were deployed along with LDPE (**Figure 2**). Both

213 2010 and 2011 deployments included RM 3.5W (**Figure 2**, yellow star). Deployment took

214 place from September 2-30, 2010 (28 days), and September 1- 22, 2011 (22 days). Water cages

215 were purchased from Environmental Sampling Technologies, Inc. (St. Joseph, MO) with all

216 polymers co-deployed within the same cage, and multiple cages deployed at each site in both

217 sampling years. The deployment system consisted of an anchor, steel cable, water cages, and

218 two buoys: one for buoyancy, and another on top for retrieval (Sethajintanin and Anderson,

219 2006). Each cage was approximately 2.5 meters off the bottom of the river.
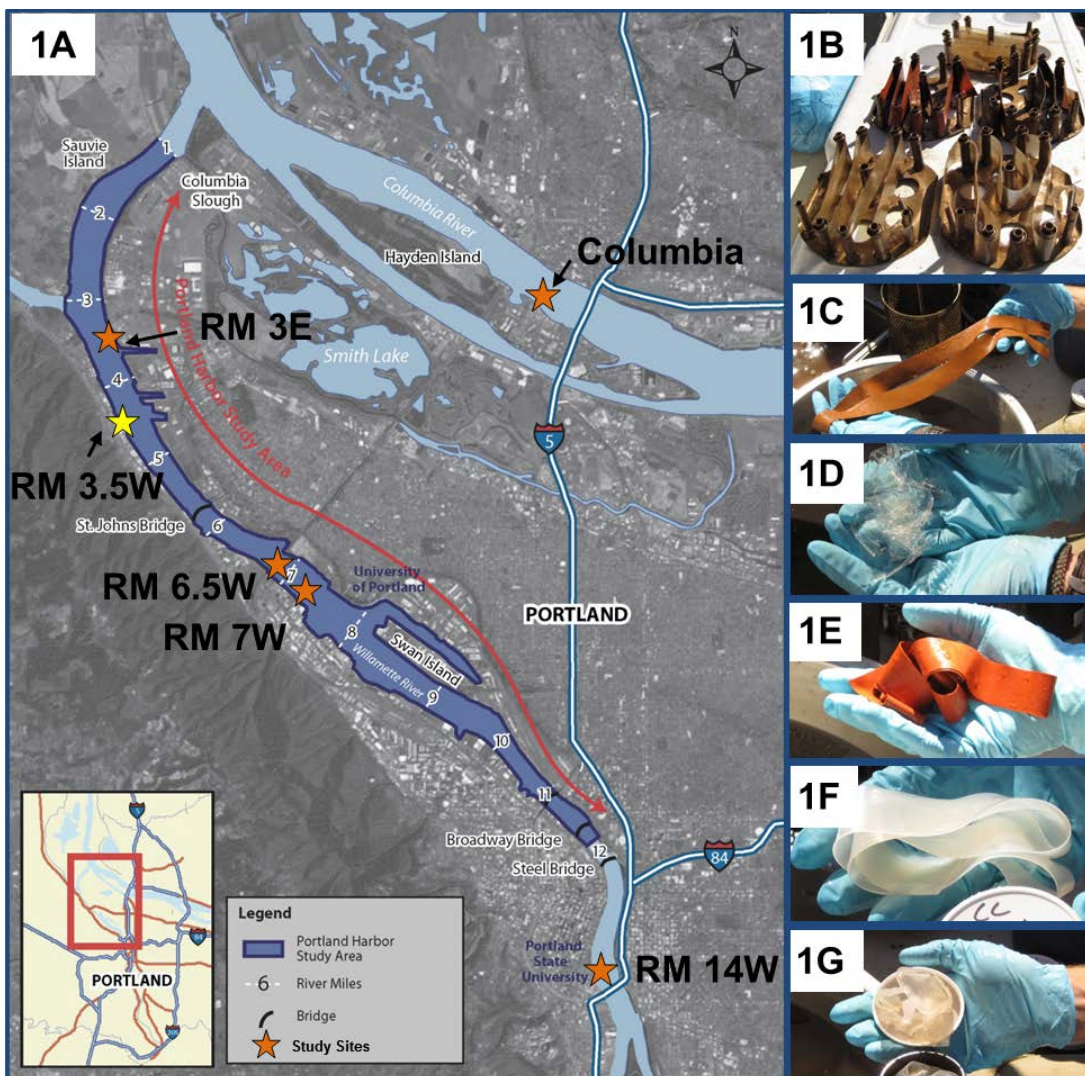
Figure 1. Field deployment of multiple polymers in Portland Harbor Superfund, OR: 1A) *stars* represent field sites in and outside of the Superfund in 2011, and the *yellow star* (RM 3.5W) was a deployment site in 2010 and 2011; 1B) silicone polymers immediately after deployment in 2010; 1C-G) polymers after deployment before storage in amber jars: SS, ST, CS, CT, AA, respectively, see table 1 for abbreviations. Map of Portland Harbor Superfund courtesy of U.S. Environmental Protection Agency.

Analytical methods

Specific method details can be found for PAH (Allan et al., 2012), OPAH (O'Connell et al., 2013), and pesticide (Anderson et al., 2014) analyses published previously. Internal standards for each method were spiked into extract aliquots just prior to instrumental analyses. A gas chromatograph (GC) with an Agilent DB-5 column (30 m length, 0.25 mm inner diameter, 0.25

234 μm film thickness) was used to analyze OPAHs and PAHs (2010 deployment), while an Agilent

235 DB-XLB (30m, 0.25mm, 0.25 μm) and a DB-17MS (30m, 0.25mm, 0.25 μm) was used to

236 analyze pesticides with dual column confirmation (Anderson et al., 2014). An Agilent Select

237 PAH column (30m, 0.25mm, 0.15 μm) was used for PAHs in the 2011 deployment. The OPAH

238 and PAH methods used mass spectrometry (MS) detection (model 5975B, Agilent), while the

239 pesticide method utilized dual electron capture detection (model 6890N, Agilent). All

240 compounds were calibrated with calibration curves of five points or more, and had correlations

241 of 0.99 or better. Contaminant screening for additional compounds was performed with GC/MS

242 retention time locking Automated Mass Deconvolution Identification Software (AMDIS) in

243 conjunction with created and purchased libraries totaling 1,180 unique compounds.

244 Identification and confirmation criteria has been described previously (O'Connell et al., 2014),

245 but each compound had at least a 60% spectral match before additional confirmation criteria

246 were used for each qualitative determination. Any compounds indentified in blank samplers

247 were removed from data described below or presented in the Supporting Information.

248

249 *Quality Control*

250 Including field, laboratory, cleaning, and instrumental blanks, over 40% of the analyzed samples

251 were for quality control (QC) purposes. During polymer construction, at least two strips were

252 analyzed from each batch to assess adequate removal of chromatographic interferences. If the

253 highest background peak had an area less than 15 fold of a 500 ng/mL spiked internal standard,

254 then that background level was considered adequate. Both strips had to pass this criterion to

255 allow a polymer batch to be used. During PRC infusion, five strips of each polymer type were

256 set aside to determine an average initial concentration of each PRC prior to deployment. Each

257 trip to Portland Harbor included field blanks to monitor contamination from travel or field

258 processing. During post-deployment cleaning, non-deployed strips were used to monitor any

259 contamination prior to freezer storage (-20 °C). When samples were extracted, laboratory

260 reagent blanks accompanied each batch or day of extraction. The final type of QC samples was a

261 verification standard, which included all target compounds for the appropriate method.

262 Compounds were verified +/- 20% of the true value for at least 90% of the target list before

263 samples were analyzed. The reporting limit was set as the average of all blank samples from

264 field and laboratory plus three times the standard deviation. Concentrations below the reporting

265 limits were not included in results.

266

267

268 *Calculated Water Concentrations*

269 For the final comparison, water concentrations were derived using empirical models with the

270 most optimal silicone and LDPE for PAHs and OPAHs. Typically for LDPE and silicone,

271 sampling rates (R_s) are determined through *in-situ* calibration with PRCs (Booij et al., 2002;

272 Huckins et al., 2002). Partition coefficients (K_{sw}) for PAHs were obtained from the literature for

273 LDPE (Choi et al., 2013) and for the final silicone that was the most similar in density and

274 thickness to the silicone used in previous work, "Silastic A" (Smedes et al., 2009). Because

275 there is not a compound specific model for estimating OPAH partition coefficients, PAH models

276 based on K_{ow} were used since that parameter would be more sensitive to OPAH compounds than

277 molecular weight (ex: log K_{ow}s: OPAHs - 0.2 to 5.3; PAHs – 3.3 to 7.3, MW: OPAHs - 108 to

278 282; PAHs – 128 to 302). All partition coefficient models have above 0.88 r^2 correlations

279 whether K_{ow} or molecular weight chemical parameters were used (Smedes et al., 2009; Choi et

280   al., 2013). For LDPE sampling rate (R_s) estimates, we used an empirical uptake theory with

281   compound-specific adjustments for target compounds (Huckins et al., 2006). Compound-

282   specific adjustments for target compounds from PRC sampling rates were based on a model

283   using over 400 data points from several compound classes and various deployments to give an

284   averaged adjustment to each analyte (see SI-Equation 3-4). However, this model was originally

285   based on LDPE filled with triolein (called semi-permeable membrane devices, or SPMDs) and

286   despite previous work showing little difference in sampling rates between SPMDs and LDPE

287   (Booij et al., 2003), it is acknowledged that future adjustments might be improved by repeating

288   this model with LDPE once enough published data is available. Silicone R_s values were

289   estimated from an empirical model as well (Rusina et al., 2009). This model uses a constant (β)

290   derived from PRC dissipation over the sampling period that is then applied for each target

291   analyte coupled with K_{sw} values to result in unique R_s estimates (see SI-Equation 5). Final water

292   concentrations for either polymer were determined making no assumptions about stages of

293   uptake at time of retrieval and used the same final equation (SI-Equation 6, Huckins et al., 2006).

294   Additional details concerning equations and models are given in the Supporting Information.

295

RESULTS AND DISCUSSION

297   *Laboratory Optimization of Silicone*

298   Silicone background was reduced to similar levels as in LDPE, but the process was iterative (see

299   Supporting Information for more details). Although polymer cleaning results are rarely reported,

300   this methodology compares well with others that rely on solvent exchanges (Booij et al., 2002;

301   Rusina et al., 2007; Schafer et al., 2010), and it is faster ($\leq$ 48h) than soxhlet extraction methods

302   (90h) (Yates et al., 2007; Monteyne et al., 2013). Moreover, solvents could be effectively

303   recycled (both hexane/ethyl acetate and methanol/ethyl acetate mixtures) between batches of

304   silicone (**SI-Figure 1B**). By using this recycled solvent, the total solvent use is reduced by 20%

305   (**SI-Figure 2**). In addition, the background of SS silicone utilizing the recycled solvent method

306   was similar to LDPE (**SI-Figure 1B** – green and black chromatograms, respectively). An

307   additional benefit is that the optimal background is achieved without relying on post-extraction

308   silica cleanup used in other silicone work (Booij et al., 2002; Allan et al., 2009; Monteyne et al.,

309   2013), and the silicone extract can be easily integrated into zebrafish bioassays (manuscript in

310   preparation).

311

312   The PRC infusion process resulted in excellent precision across the five different strips set aside

313   to determine initial PRC concentrations, and were extracted over two different days. The average

314   relative standard deviations (RSDs) of these samples were <13% for all four PRCs. The

315   repeatability compares well with other published infusion RSDs of 10% or less (Booij et al.,

316   2002). The efficiency of the infusion after modifying the methanol/water ratio was calculated by

317   dividing the average amount in the silicone by the amount in the initial infusion solution.

318   Infusion efficiencies of PRCs ranged from 20 ± 7 % (9,10-anthraquinone-d8) to $111 \pm 11\%$

319   (p,p'-DDE-d4), indicating that the infusion process was successful transferring most, if not all, of

320   the compounds into silicone strips. Extraction efficiencies were not measured in this study, but

321   assumed to be adequate and similar to the 96% extraction efficiency reported from our group

322   using other silicone with the same methodology for PAHs (O'Connell et al., 2014).

323

324   *Initial Field Comparison of Five Silicones*

325   During field retrieval, all silicone polymers had minimal biofouling after a few seconds of

326   physical agitation with ambient water (**Figure 1C-G**). In total, 25 PAHs were identified among

327   all polymers (**Figure 2**). Polymers were first compared using PAHs due to analytical methods

328   available at that time, and since PAHs are still contaminants of concern in Portland Harbor

329   (Sower and Anderson, 2008). Concentrations were normalized for each silicone by mass so

330   differences in volume between polymers would not confound comparisons. AA sequestered

331   roughly 2 fold more ΣPAHs than other silicone polymers (**Figure 2**). However, both AA and CT

332   silicone were heavily degraded during the extraction process, leaving behind silicone residue in

333   both glassware and instrumentation. The leftover residue likely resulted in the very low PAH

334   surrogate recoveries seen for both AA (2-11%) and CT (2-43%), which contrasts with the higher

335   recoveries seen with ST (70-130%), SS (62-138%), and CS (73-130%). Despite the common use

336   of AA as a silicone PSD (Rusina et al., 2007; Yates et al., 2007; Rusina et al., 2009; Smedes et

337   al., 2009), the other types of silicone were substantially easier to extract, and resulted in better

338   recoveries and precision of analytes (**Figure 2**). The siloxane background of AA and CT also

339   interfered with full scan analyses. Therefore, only ST, SS, and CS were further evaluated for

340   qualitative sensitivity of low K_{ow} compounds which can be seen in the Supporting Information.

341   Overall, 30 compounds were identified between polymers (**Table S3**), and LDPE did not

342   sequester any compounds below a log K_{ow} value of 4.9, which is similar to previous field data

343   (Allan et al., 2010; Allan et al., 2013). Because sequestration was similar between the three

344   silicones and advantages among them were not immediately apparent, ST, SS, and CS were

345   deployed along with LDPE the following year.
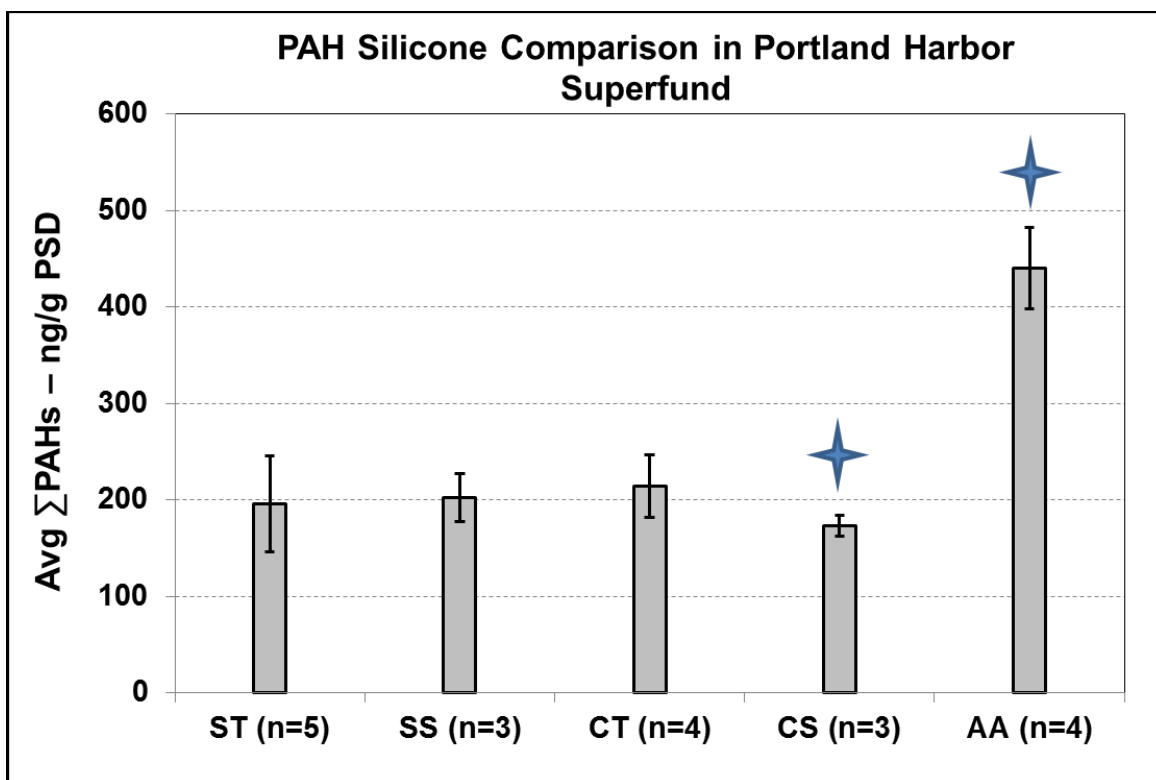
17

Figure 2. Average summation of 25 PAHs from all silicone in 2010 at RM 3.5W. Concentrations were normalized to polymer mass to highlight differences between silicone polymers. Blue stars indicate severe degradation of polymer during extraction.

Quantitative Surrogate Recoveries and Ideal Silicone Polymer Selection

Six different field sites were sampled using LDPE, SS, ST, and CS polymers to further assess

and compare silicones to LDPE. Samples were analyzed using quantitative methods for PAHs,

OPAHs, and pesticides (see **Table S1**). Laboratory surrogate recoveries after extraction varied

widely among each method. For silicones, pesticide recoveries ranged from 13-113%, averaging

60%. PAH recoveries ranged from 35-185%, and averaged 94%. OPAH recoveries performed

well, ranging from 72-140% with an average of 105%. Recoveries of surrogates in LDPE

extractions were similar for pesticides (34-86%) and PAHs (30-98%), and like silicone, the best

recoveries were for OPAHs, which ranged from 69-110% with an average of 88%. Lower

recoveries (outside of $\pm$ 30% of the true value) were almost always associated with more volatile

362   surrogates. For instance, most low recoveries for PAHs were for naphthalene-d8, and for

363   pesticides, all low recoveries were attributed to tetrachloro-m-xylene. Additional variability may

364   be due to the study size (> 70 samples) and multiple weeks of extractions. However, most

365   recoveries were within 30% of the true value, and for comparison purposes, recoveries were

366   similar for each method across polymers, so concentrations were assumed to be affected

367   similarly across the values reported below.

368

369   Concentrations of three pesticides identified in Portland Harbor predictably differed between

370   LDPE and silicone based on log K_{ow}, and were consistent with earlier AMDIS results.

371   Specifically, **Figure 3** illustrates all silicones having greater amounts sequestered (ng/g PSD) of

372   endosulfan sulfate (log K_{ow} 3.7) compared with LDPE. This is in contrast with p,p'-DDD, which

373   was greater in LDPE and more hydrophobic (log K_{ow} 6.0). Chlorpyrifos was more variable

374   among the polymers (**Figure 3**), with a log K_{ow} (4.96) value between that of the other

375   compounds. One goal of this research was to develop samplers for co-deployment, and the

376   pesticide and AMDIS data suggests that the methodology successfully exploited inherent

377   differences in polymers initially reported in other work (Rusina et al., 2007; Allan et al., 2013).

378   While ST had the highest amount of endosulfan sulfate sequestered in the polymer, it was more

379   difficult to use in the field and laboratory due to a tendency to adhere to metal and glass surfaces

380   when dry, and had higher variability within a complementary range of K_{ow} sequestration (**Figure

381   3**). Therefore, SS silicone was chosen as the best silicone coupled with LDPE since it had the

382   highest precision across all field testing and chemical compound classes. However, it is

383   acknowledged that there is little difference between either silicone sponge material overall (SS or

384   CS).

Pesticide Polymer Comparison
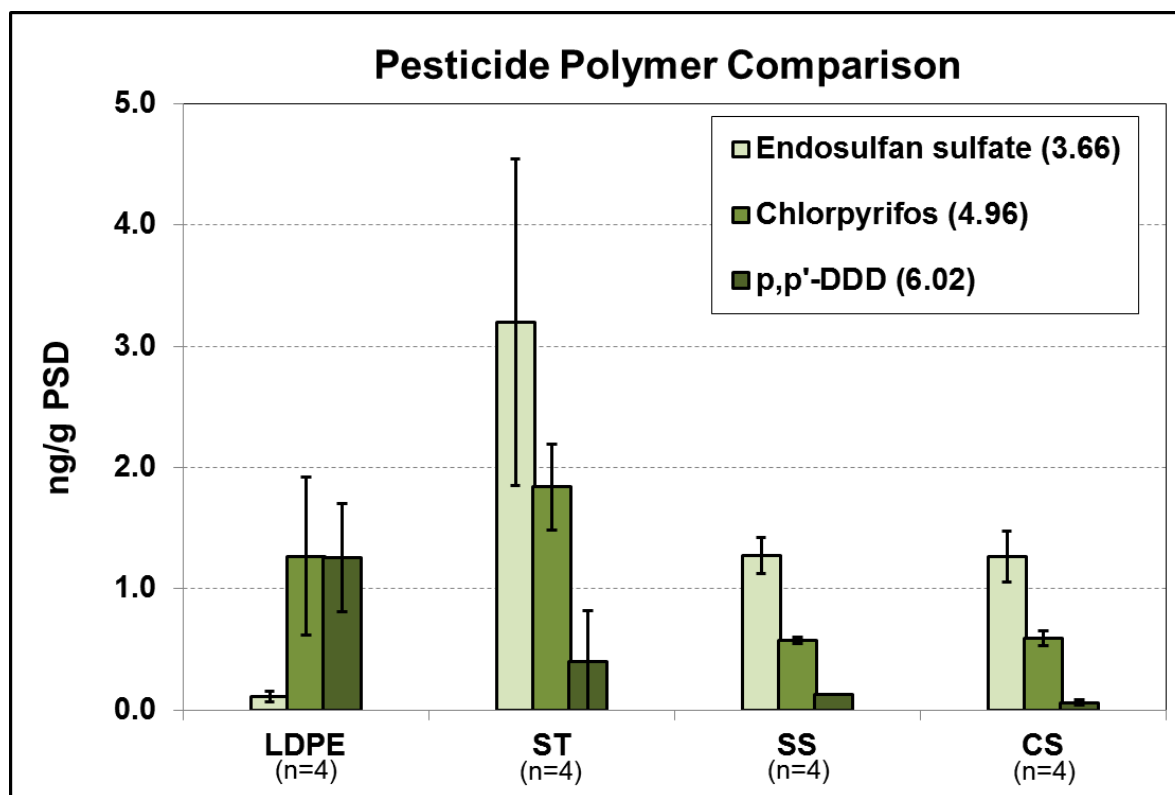
Figure 3. Average concentrations of three pesticides found in Portland Harbor RM 14W, 2011. Concentrations are normalized per mass of each PSD to highlight sequestration differences. Numbers in parentheses after compound names represent log K_{ow} values.

Final Polymer Comparisons for PAHs using Normalized and Water Calculated Data

In the last comparison using SS silicone and LDPE, PAH data was evaluated to see if differences

in absorption or extraction methodology would be reconciled after calculations to water

concentrations. In **Figure 4A**, ΣPAH concentrations in the SS silicone polymer (ng/g) are about

7 fold lower than in LDPE. While acknowledging differences in solvents which could impact

extraction efficiency, this was surprising considering previous evidence showing much higher

concentrations of PAHs in silicone over LDPE (Allan et al., 2013). Regardless, overall

differences were reconciled to average 3.5-fold or less (individual or ΣPAH) once both polymer

extracts were calculated to water concentrations in ng/L (**Figure 4A**). Moreover, this nominal 3-

400   fold difference is consistent with other PAH silicone and LDPE data from aqueous field

401   deployments (Allan et al., 2013). LDPE is clearly the better polymer for PAHs using this

402   methodology, as it sequesters PAHs at higher concentrations and likely has more accurate results

403   than silicone given the polymer-specific partition coefficients for polyethylene. Although

404   silicone partitioning coefficients were shown to vary little (on a log scale) in a multi-silicone

405   comparison (Smedes et al., 2009), small differences in these estimates could explain the gap in

406   quantitation for this work. Future work would be improved by empirically determining K_{sw}s for

407   SS silicone. Overall, both polymers consistently sequestered 17 PAHs of varied molecular size

408   and physicochemistry (log K_{ow} range: phenanthrene – 4.56 to indeno(1,2,3-c,d)pyrene - 6.58).

409   The ratio of individual analytes was conserved between polymers, with phenanthrene,

410   fluoranthene, and pyrene comprising the majority of ΣPAH amounts (56 to 84% in silicone, 67 to

411   81% in LDPE). Although LDPE sequesters more PAHs, both polymers in this field study would

412   have resulted in similar descriptions of field sites if used solely for Portland Harbor

413   characterization. Both polymers showed elevated levels of PAHs within the Superfund (sites

414   RM 3E to 7W) as compared to outside the area (Columbia and RM 14W sites, **Figure 4A**).

415   Results of replication are also similar (**SI-Figure 3A**), with RSDs averaging 7% for LDPE and

416   11% for SS silicone across field sites.
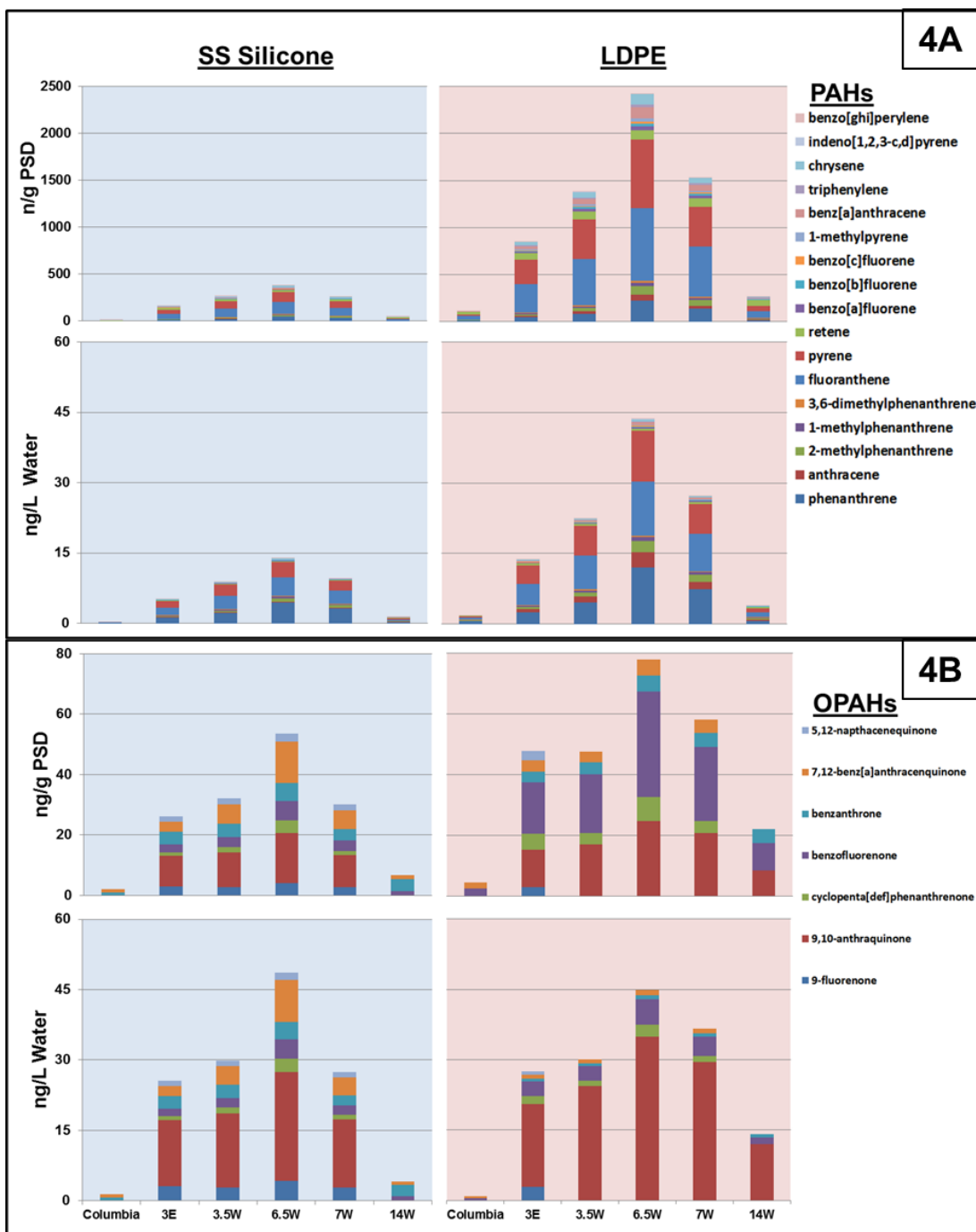
Figure 4. Average (n=3) individual PAH and OPAH concentrations before (ng/g PSD) and after deriving freely dissolved water calculations (ng/L) for SS Silicone (blue background) and LDPE (light red background) for six Portland Harbor sites in 2011. 4A) PAH concentrations are consistently higher in LDPE before and after back-calculation although individual contributions are similar. 4B) OPAH concentrations are more similar than PAHs before and especially after back-calculation between polymers, although individual contributions are more disparate. Fluorenone and 5,12-napthacenequinone are below the reporting limit for LDPE at all sites except RM 3E.

Final Polymer Comparisons with Emerging Oxygenated-PAHs

428 OPAHs are an emerging concern in PAH contaminated areas (Lundstedt et al., 2007), and

429 represent a good example of the physicochemistry range that might be sensitive to differences

430 between silicone and LDPE (log K_{ow} 0.2 – 5.3). The data in **Figure 4B** represents some of the

431 first aqueous concentrations of OPAHs at a Superfund site using passive samplers, and includes

432 evidence showing OPAHs having similar magnitudes to PAHs in Superfund waters (**Figure 4**).

433 Comparisons between ΣPAH and ΣOPAHs have been shown to be similar among several other

434 matrices (Layshock et al., 2010), and in a very recent publication, concentrations of 9-fluorenone

435 and 9,10-anthraquinone were found to be higher than corresponding PAH homologues in waste,

436 river, and effluent waters (Qiao et al., 2014). Overall, contrary to our original hypothesis that

437 LDPE would not sequester OPAHs similarly to silicone, ΣOPAHs are similar with4 out of 6 sites

438 not significantly differing between polymers ($p \geq 0.44$ from t-tests, see **SI-Figure 3B**). In

439 contrast to PAHs, the amount of OPAHs sequestered in each polymer is similar despite the log

440 K_{ow} range from 3.4 (9,10-anthraquinone) to 4.8 (5,12-naphthacenequinone) (**Figure 4B**). While

441 it has long been demonstrated that K_{ow} alone cannot account for uptake differences observed in

442 model passive samplers (Huckins et al., 1999; Luellen and Shea, 2002; Huckins et al., 2004), the

443 use of additional parameters to more accurately and precisely model uptake has been elusive. As

444 an example, out of several physiochemical parameters (molecular weight, polar surface area,

445 Van der Waals volume, C:H ratio), a regression using K_{ow} to predict OPAH sequestration has a

446 model coefficient (R^2) of just 0.08, while one using a ratio of Van der Waals volume over the

447 polar surface area is a slightly better predictor of partitioning ($R^2 = 0.20$, see **SI-Figure 4**). In

448 other work, larger molecular size was found to possibly contribute to differences in compound

449 diffusivity between LDPE and silicone (Allan et al., 2013). Clearly, more work is needed to

450   predict absorption between polymers, but future studies might benefit from using these or other

451   physiochemical parameters.

452

453   Perhaps the most interesting OPAH results are differences observed between polymers for

454   individual OPAH concentrations. Specifically, benzofluorenone and 7,12-

455   benz[a]anthracenequinone (**Figure 4B**) differed dramatically between polymers by 50% and

456   109%, respectively. Differences persist even after calculating water concentrations, but

457   determining specific partitioning coefficients might rectify some of these discrepancies. Like the

458   ΣPAHs, the ΣOPAHs from either polymer suggest higher concentrations within the Superfund

459   site than outside of it. However, individual contributions to these ΣOPAHs would indicate that

460   9,10-anthraquinone and benzofluorenone would be the primary components based on LDPE

461   results (averaging 83% of the total), while no individual OPAH comprised more than 25% of

462   ΣOPAHs in SS silicone. Four to five individual OPAHs are needed to achieve 83% or more of

463   ΣOPAHs in the silicone at any site. In this respect, the original hypothesis is partially supported

464   because silicone sequesters more individual OPAHs than LDPE. In fact, fluorenone and 5,12-

465   napthacenequinone are below the reporting limit for LDPE at all sites except RM 3E. The

466   difference between polymers is critical, because early evidence suggests that there are large

467   differences between individual OPAH toxicities (Knecht et al., 2013). If remediation or toxicity

468   concerns are important at a contaminated area, then methods that capture a large range of

469   individual OPAHs will have additional value. Ultimately, both PAHs and OPAHs were

470   quantitated using both polymers, but silicone appears more appropriate for OPAHs given the

471   greater sensitivity for individual compounds (especially 9-fluorenone, benzanthrone, and 5,12-

472   naphtacenequinone).   This work advances methods for using silicone passive samplers alone or

473   in conjunction with LDPE, provides information on analytical criteria for passive sampling

474   choices, and provides valuable real world OPAH information for this emerging compound class.

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