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Huysman, S., Vanryckeghem, F., De Paepe, E., Smedes, F., Haughey, S. A., Elliott, C. T., Demeestere, K., & Vanhaecke, L. (2019). Hydrophilic divinylbenzene for equilibrium sorption of emerging organic contaminants in aquatic matrices. *Environmental science & technology*. Advance online publication. <https://doi.org/10.1021/acs.est.9b01814>

Published in:

Environmental science & technology

Document Version:

Peer reviewed version

Queen's University Belfast - Research Portal:

[Link to publication record in Queen's University Belfast Research Portal](#)

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1 Hydrophilic divinylbenzene for equilibrium sorption
2 of emerging organic contaminants in aquatic
3 matrices

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15
16 KEYWORDS

17 emerging organic contaminants; hydrophilic DVB; water; equilibrium partitioning; sorption;
18 sampling

19 ABSTRACT

20 Hydrophilic divinylbenzene (DVB) (Bakerbond™) has surfaced as a promising sorbent for
21 active sampling of analytes from aqueous matrices over a very broad polarity range. Given this,
22 hydrophilic DVB may likewise offer potential for passive sampling, if sorbent-water partitioning
23 coefficients (K_{sw}) were to be available. In this work, static exposure batch experiments were
24 performed to quantitatively study the equilibrium sorption of 131 environmentally relevant organic
25 contaminants (P values ranging from -1.30 to 9.85) on hydrophilic DVB. The superior affinity of
26 hydrophilic DVB, as compared to Oasis HLB, for compounds with a broad polarity range was
27 confirmed by functional FTIR and Raman characterization, demonstrating the presence of
28 carboxyl moieties. Concentration effects were studied by increasing compound concentrations in
29 mixture experiments, and resulted for the steroidal EDCs in higher K_{sw} , while lower K_{sw} were
30 obtained for the (alkyl)phenols, personal care products, pesticides, pharmaceuticals and phthalates.
31 Nevertheless, K_{sw} remained constant in said design for equilibrium water concentrations at
32 environmentally relevant seawater levels. Independent analysis of thermodynamic parameters
33 (change in enthalpy, entropy and Gibbs free energy) revealed the nature of the main partitioning
34 processes. While polar ($\log P < 4$) compounds were mainly served by physisorption, non-polar
35 ($\log P > 4$) compounds also exhibited binding by multiple hydrogen bonding. In conclusion, this
36 research facilitates the future application of hydrophilic DVB for active as well as passive
37 sampling in the analysis of organic contaminants for monitoring purposes but also for toxicity
38 testing.

39

40 INTRODUCTION

41 The ever-increasing number of emerging contaminants released into our (aquatic) environment
42 stresses the need for the deployment of efficient monitoring strategies ¹. In this context, the use of
43 polymeric sorbents has surfaced as a highly valuable strategy for active and passive sampling of
44 organic compounds from aquatic matrices ^{2,3}. In active sampling, polymeric sorbents are widely
45 used in solid-phase extraction (SPE) cartridges for the enrichment of contaminants and/or clean-
46 up of aquatic matrices ². In recent years, however, the number of publications on the application
47 of polymeric sorbents and materials in passive sampling studies is steadily increasing.

48 At present, a number of polymeric materials have been applied for the monitoring of emerging
49 contaminants using passive sampling based approaches ^{3,4}. However, most studies focus on
50 specific polymeric passive samplers efficiently binding compounds within a specific polarity range
51 ⁵. In passive sampling, the function of a sampler as an infinite sink is determined by the affinity
52 towards the envisaged analytes, which is governed by the polarity, (inversely related to log P) and
53 chemical functionalities of both. Indeed, silicones (mainly polydimethylsiloxane, PDMS) invoke
54 the uptake of non-polar chemicals (log P > 4) ^{6,7}, while Chemcatchers® SDB-RPS (sulfonated
55 divinylbenzene - reversed phase sulfonate) mainly accumulate more polar chemicals (log P < 4)
56 and Chemcatchers® C₁₈ sample compounds ranging from moderately polar to moderately non-
57 polar, i.e. log P ranging between 0.9 and 5.8 ^{8,9}. In this context, the Oasis HLB® co-polymer has
58 gained in popularity and was recently incorporated in different POCIS configurations ^{10,11}, as it
59 permits the accumulation of very polar to moderately non-polar compounds (log P ranging from -
60 1.6 up to 5) ¹². Its affinity towards hydrophobic compounds (log P > 5) however still remains a
61 hurdle ⁵. In this work, we propose hydrophilic DVB as a sorbent for sampling a broad range of
62 emerging contaminants. Although hydrophilic modified DVB materials have been applied earlier
63 as solid phase microextraction fibers, blades and membranes ¹³⁻¹⁵, the potential of hydrophilic

64 DVB for passive sampling of such a broad range of emerging contaminants remains underexplored
65 as opposed to the frequently applied Oasis HLB® sorbent. Moreover, higher extraction
66 efficiencies were obtained using hydrophilic DVB for non-polar compounds ($\log P > 4$) during
67 active sampling as compared to Oasis HLB®¹⁶. Hence, investigating the underlying mechanisms
68 of said hydrophilic DVB sorbent in both active (SPE) and passive sampling seems promising.
69 Indeed, there is no information available on the surface chemistry (functional groups, pore size
70 and particle size distribution) of hydrophilic DVB neither on the partitioning behaviour of organic
71 contaminants between water and hydrophilic DVB¹⁷. Furthermore, hydrophilic DVB is
72 commercially available in a robust housing, i.e. Bakerbond Speedisks®, which simplifies its
73 application for passive sampling of the aquatic environment.

74 Therefore, the goal of this work was to investigate the equilibrium sorption behaviour of a broad
75 range of aqueous organic contaminants on freely dispersed hydrophilic DVB sorbent. The specific
76 objectives included (i) revealing the surface chemistry of hydrophilic DVB, (ii) determining the
77 K_{sw} of a mixture of 131 environmentally relevant organic contaminants at field concentrations,
78 (iii) examining sorption linearity of the target organic contaminants by increasing compound
79 concentrations, and (iv) assessing the impact of relevant environmental parameters (i.e.
80 temperature, pH and salinity) on K_{sw} . Ultimately, this research intends to reveal the underlying
81 mechanisms of hydrophilic DVB sorption in active and passive sampling.

82

83 MATERIALS AND METHODS

84 **Chemicals and materials.** In this study, standards of 131 environmentally relevant organic
85 contaminants ($\log P$ ranging from -1.30 to 9.85, depicted in Table S1) were purchased at Bayer
86 (Germany), Fluka (Belgium), Sigma Aldrich (St. Louis, MO, USA), Steraloids Inc (Newport, RI,

87 USA), Lipomed GmbH (Germany), MpBio (Belgium) and TRC (Canada), covering 6 major
88 classes, i.e. 4 alkylphenols, 5 personal care products, 25 pesticides, 32 pharmaceuticals, 15
89 phthalates and 50 steroidal endocrine disrupting compounds (EDCs). The selected organic
90 contaminants were based on legislative frameworks and directives for protecting surface and
91 marine waters, i.e. the U.S. Clean Water Act, the EU WFD watchlist, OSPAR, Reach and Norman
92 ¹⁸⁻²². Primary stock solutions and standard mixtures were prepared in pure methanol (CH₃OH) or
93 in a mixture of methanol/water (10/90, v/v %) with 0.1% (v/v %) formic acid and 0.1 g L⁻¹
94 Na₂EDTA.2H₂O, the latter only for pesticides, pharmaceuticals and personal care products,
95 thereby attaining concentrations between 0.01 and 1000 ng μL⁻¹. Solutions were stored in dark
96 glass bottles at -20°C. Organic solvents were of Optima UPLC-MS grade, purchased from Fisher
97 Scientific (Loughborough, UK). The inorganic salts, used to prepare reference seawater, were
98 supplied by Sigma Aldrich (St. Louis, MO, USA) and processed according to ASTM D-1141 ²³.
99 The hydrophilic divinylbenzene (DVB) Speedisks® and Oasis® HLB cartridges (200 and 500 mg)
100 were purchased from Filterservice (Eupen, Belgium) and Waters (Brussels, Belgium),
101 respectively.

102 **Static exposure batch experiments.** A classic static exposure batch system, which has
103 previously been applied for passive sampling studies ^{24,25}, was established under controlled
104 conditions of continuous stirring (100 rpm), temperature (experiment dependent) and absence of
105 light. The latter was applied to determine the K_{sw} of a mixture of the 131 selected contaminants
106 between artificial seawater and the hydrophilic DVB sorbent. It was also studied how compound
107 concentration and environmental parameters affect the K_{sw}-values. Aqueous suspensions,
108 containing 25 mg of freely dispersed hydrophilic DVB sorbent L⁻¹ were used in all batch
109 experiments. The DVB sorbent has a pore size of 200 Å and a particle size between 12 and 42 μm

110 (for 95% of the particles) as demonstrated in Figure S1. The sorbent/water-ratio was determined
111 based on preliminary experiments. A higher sorbent/water-ratio disabled us to quantify the spiked
112 compounds, as aqueous equilibrium concentrations were below the analytical detection limits.
113 Compound mixtures were spiked in 1L glass beakers closed with aluminium foil ²⁶ to prevent
114 evaporation. At the end of each batch test, the beaker's content, containing both the aqueous and
115 sorbent phases, was filtered over a Whatman GF/D glass fibre filter coupled in series with a packed
116 SPE cartridge to extract the analytes from the aqueous phase (see supplementary information,
117 Figure S 2). The glass fibre filter with sorbent phase and packed SPE cartridge were separately
118 eluted and analysed, to provide sorbent and aqueous concentrations, respectively. The subsequent
119 sample preparation and analysis were optimised for the different compound groups of interest (see
120 sample analysis). Furthermore, to evaluate potential adsorption to glass walls and/or hydrolysis of
121 the spiked compounds during batch experiments, reference glass beakers were included in the
122 experimental set-up. These reference glass beakers, containing only water at the initial nominal
123 concentrations of the selected compounds and no sorbent, were subjected to similar conditions as
124 beakers containing the spiked compounds with sorbent. In addition, blank samples were also
125 examined and used for adjusting K_{sw} .

126 **Experimental determination of K_{sw} .** The K_{sw} were determined at neutral pH conditions and at
127 a temperature of 8°C. The spike concentration for the target compounds was based on
128 environmentally relevant levels but sufficiently high as to enable measurements above the
129 methods' detection limits after sorbent sorption. As such, the initial nominal concentration was set
130 at 1.5 nmol L⁻¹ for each compound. The residual concentrations in water and the amounts
131 accumulated by the sorbent were measured at 0, 1, 2, 4, 6, 8, 12, 24, 48, 96 and 168h. These

132 experimental times were selected to evaluate whether equilibrium was reached within one day or
133 one week.

134 **Partitioning at different compound concentrations.** To investigate the effect of compound
135 concentration on the K_{sw} , at a contact time of 48h, multiple equilibrations were performed under
136 similar conditions at various concentration levels, i.e. 0.75, 1.5, 3.0, 6.0, 12, 24 and 48 nmol L⁻¹.
137 This experiment was executed at a water temperature of 8°C and under neutral pH conditions.

138 **Partitioning under different environmental conditions.** To evaluate the impact of varying
139 environmental conditions on the K_{sw} (48h contact time), three parameters were investigated within
140 environmental relevant ranges, i.e. pH, temperature and salinity respectively ranging from 5 to 8,
141 from 4 to 16°C, and from 0 to 35 psu. Response surface modelling (RSM), and more specifically
142 the Box-Behnken experimental design, enabled to fit quadratic models to the experimental log
143 K_{sw} , which contained main, quadratic and interaction factors related to the selected environmental
144 parameters.

145 **Analytical methods. Sorbent characterization.** Sorbent characterization was performed to
146 reveal the chemical properties of the hydrophilic DVB surface and to compare the latter with the
147 frequently used Oasis HLB[®]. This was achieved by the use of a Thermo Scientific Nicolet iS50
148 spectrophotometer (Thermo Fisher Scientific, Dublin, Ireland) to obtain the FTIR (Fourier
149 transform infrared), Raman and NIR (Near-infrared) spectra within the range of 400 - 4000 cm⁻¹,
150 400 - 4000 cm⁻¹ and 3000 – 12000 cm⁻¹, respectively. Other acquisition parameters were: number
151 of scans: 256, number of background scans: 256, background gain: 4.0, and resolution: 4.0 (FTIR
152 and NIR) / 8.0 (Raman). Acquisition was repeated 3 times, and spectral data were averaged prior
153 to further data processing.

154 *Sample analysis.* Organic contaminant quantification in the aqueous and sorbent phases was
155 performed using three in-house developed and validated analytical methods, consisting of the
156 appropriate extraction followed by an optimized UHPLC-HR-Q-Orbitrap™-MS methodology.
157 Chromatographic separation was achieved using reversed phase chromatography with gradient
158 elution using a Hypersil Gold column (1.9 μm, 50/100 x 2.1 mm). Analyte detection was carried
159 out on a Q-Exactive™ benchtop HRMS (Thermo Fisher Scientific, San-Francisco, USA). Details
160 regarding the sample analysis have been published earlier^{16,26,27}, and only the main differences
161 are briefly described in the supplementary information. In short, the residual water concentrations
162 for the steroidal EDCs were determined by extracting with Bakerbond Hydrophilic DVB
163 Speedisks, while the personal care products, pesticides, pharmaceuticals, (alkyl)phenols and
164 phthalates were extracted by using Oasis®HLB. These analytical methods exhibited excellent
165 performance; i.e. repeatability and precision below 20 % RSD, relative recovery between 80 - 120
166 %, and good linearity ($R^2 > 0.99$ and no lack-of-fit).

167 **Data treatment and analysis.** Spectroscopic data were extracted from the FTIR, Raman and
168 NIR using TQ Analyst 8.6.12 (Thermo Fisher Scientific, Dublin, Ireland). Targeted processing of
169 full-scan data, obtained by the Q-Exactive HRMS, including the identification and quantification
170 of target compounds, was executed by XCalibur™ 4.0 software (Thermo Fisher Scientific). The
171 software program JMP 12.0 (SAS Institute Inc, Cary, USA) was used to evaluate and model the
172 appropriate RSM design Box-Behnken Design. Graphics were produced by using R (Version 3.4).

173 *Determination of K_{sw} .* K_{sw} was determined using the above-described static exposure design and
174 calculated by eq 1, i.e. absolute mass concentration measured in the water (N_w ; nmol) phase at
175 start conditions ($t=0$) and equilibrium ($t=\text{equilibrium}$), concentration measured in the water phase
176 at equilibrium ($C_w, t=\text{equilibrium}$; nmol L⁻¹) and the amount of sorbent (M_s ; kg).²⁸

$$K_{sw} = \frac{N_{w,0=equilibrium} - N_{w,t=equilibrium}}{C_{w,t=equilibrium} \times M_s} \quad (1)$$

178 *Adsorption modelling.* Adsorption isotherms were investigated by applying the Freundlich
 179 model (see Eq. 2)²⁹, where q_e (nmol g⁻¹) is the mass of accumulated compound by the sorbent at
 180 equilibrium, which equals $C_{s,t}$ as described under 2.4.1, K_F ((nmol g⁻¹)/(nmol L⁻¹)ⁿ) the Freundlich
 181 constant, C_e (nmol L⁻¹) the compound concentration in the water phase at equilibrium, equivalent
 182 to $C_{w,t}$ described under 2.4.2, and n the dimensionless Freundlich exponent. The thermodynamic
 183 parameters²⁹, i.e. change in Gibbs free energy ($\Delta G_{288,15K}$), enthalpy (ΔH) and entropy (ΔS), were
 184 determined using the van't Hoff (see Eq. 3) and change in Gibbs free energy equations (see Eq.
 185 4). R represents the universal gas constant (8.314 J K⁻¹ mol⁻¹) and T the absolute temperature (K).

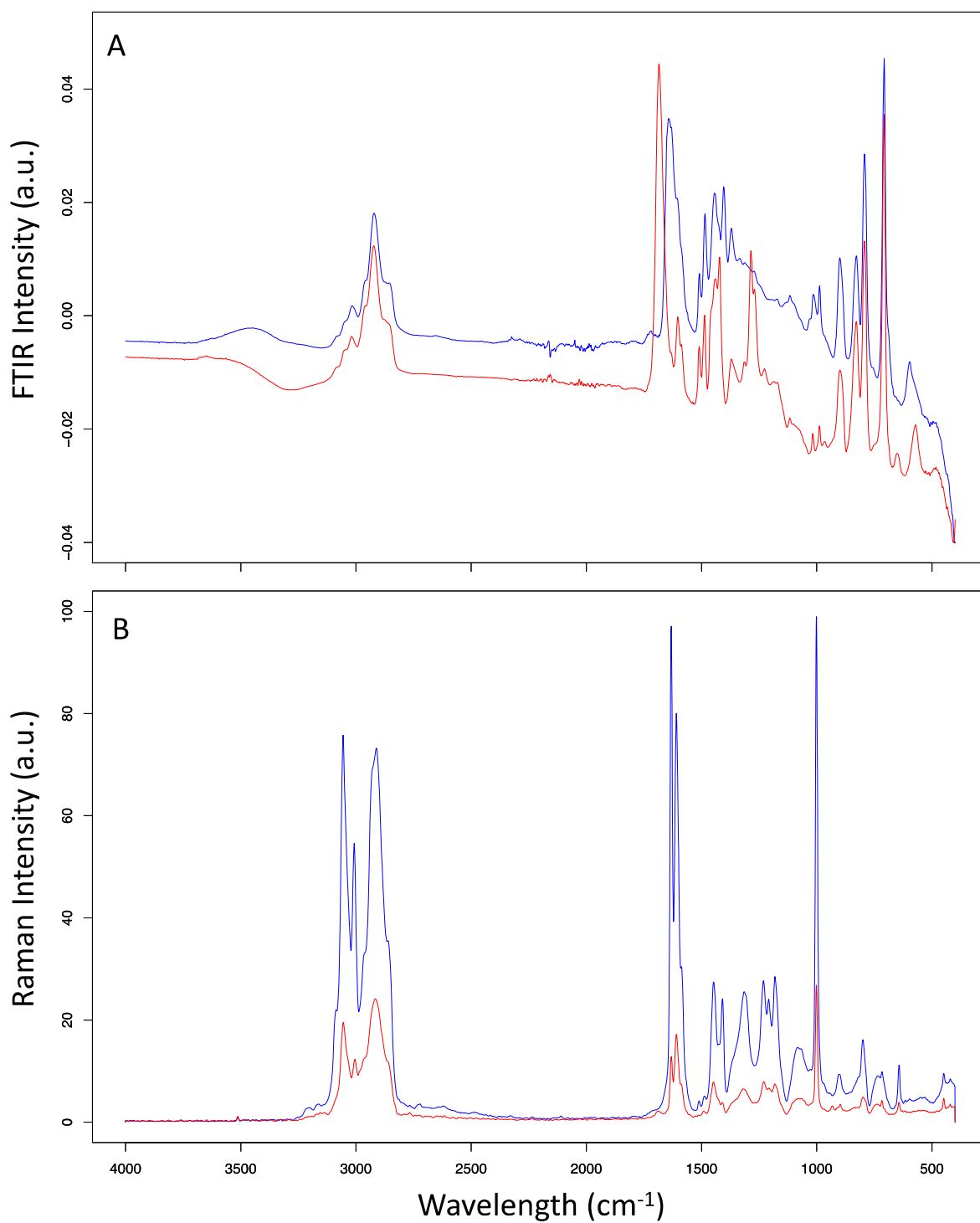
$$q_e = K_F C_e^n \quad (2)$$

$$\ln(K^\circ) = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (3)$$

$$\Delta G_{288,15K} = \Delta H^\circ - T\Delta S^\circ \quad (4)$$

189
 190 RESULTS AND DISCUSSION

191 **Sorbent characterization.** To the best of our knowledge, the surface chemistry of hydrophilic
 192 DVB has not been studied earlier. This work relied on spectral analysis (i.e. FTIR, Raman and
 193 NIR) to unravel surface functionalities of hydrophilic DVB. Additionally, the co-polymer
 194 poly(divinylbenzene-co-N-vinylpyrrolidone), also more familiar under the tradename Oasis[®]
 195 HLB, was analysed for comparison. FTIR and Raman spectra are presented in Figure 1, whilst
 196 NIR spectra can be found in supplementary Figure S3.



197

198 **Figure 1.** Averaged FTIR (A, n = 3 for each sorbent) and Raman (B, n = 3 for each sorbent)

199 spectroscopic analysis of hydrophilic DVB (Bakerbond™) (Blue) and Oasis® HLB (red).

200 Multivariate statistical analysis of the obtained FTIR spectra demonstrated significant
201 differences between the two sorbents (p -value < 0.05 , $R^2(X)(cum) = 0.989$, $R^2(Y) = 0.99$, $Q^2(cum)$
202 $= 0.974$). The main spectral differences consisted of FTIR peaks at 1642 and 1403 cm^{-1} for
203 hydrophilic DVB, and 1684 cm^{-1} for Oasis[®] HLB. An FTIR peak at 1642 cm^{-1} has been related to
204 the presence of water adsorbed to amorphous regions of a polymer^{30,31}, suggesting the presence
205 of hydroxyl [-OH] and/or ketone [-C=O] groups. The FTIR peak at 1403 cm^{-1} of hydrophilic DVB
206 represents the presence of carboxyl [-COOH] groups^{32,33}. For Oasis[®] HLB, the FTIR peak at 1684
207 cm^{-1} corresponds to the amide [C-N] stretching vibration of the pyrrolidine ring present in the PVP
208 (poly-N-vinylpyrrolidone) moiety. As no additional peak was observed at 3400 cm^{-1} and because
209 the FTIR amide peak was observed within the $1650 - 1750\text{ cm}^{-1}$ range, the presence of a tertiary
210 amide was concluded. In addition, for both sorbents, peaks at 1600 and 1510 cm^{-1} confirmed the
211 occurrence of aromatic hydrocarbons [C=C] belonging to the divinylbenzene co-polymer.
212 Complementary to the FTIR spectra, the Raman spectra also provided qualitative and quantitative
213 information on the functional groups of the two sorbents (Figure 1). Raman analysis revealed and
214 confirmed the presence of carboxyl [-COOH] moieties in the hydrophilic DVB co-polymer, i.e. a
215 peak at 1409 cm^{-1} was observed³⁴. In addition, the occurrence of the Oasis HLB[®] vinyl-groups
216 [CH₂=CH₂] was confirmed as we observed a Raman peak at 1229 cm^{-1} . Aside from the Raman
217 peaks at 1409 cm^{-1} and 1229 cm^{-1} , in general, similar spectra were observed for both the
218 hydrophilic DVB and Oasis[®] HLB co-polymers. However, more intense signals were marked for
219 the hydrophilic DVB functional groups, revealing a higher degree of cross-linkage and
220 functionalisation for hydrophilic DVB as compared to Oasis[®] HLB, offering an explanation for
221 the higher extraction efficiencies for steroidal EDCs, pharmaceuticals, pesticides and personal care
222 products that have generally been observed for hydrophilic DVB versus Oasis[®] HLB^{16,27}. No

223 significant (p-value < 0.05) differences were observed between the NIR spectra of hydrophilic
224 DVB and Oasis[®] HLB.

225 **Equilibrium partitioning between water and hydrophilic DVB. Mass balances.** The applied
226 analytical methods for the quantification of the 131 organic contaminants studied in this work, have
227 been extensively and successfully validated as reported earlier ^{16,26,27}. To assure that decreasing
228 contaminant concentrations measured in the aqueous phase during the aforementioned batch tests
229 were merely caused by sorption on the sorbent, mass balances were calculated for every
230 contaminant. This was achieved by comparing the initially spiked contaminant quantity to the sum
231 of the fractions remaining in the water and sorbent phases ³⁵. Average mass balances (%) and
232 corresponding analytical repeatabilities (% RSD) of the different time points in equilibrium
233 (constant K_{sw}) for each studied contaminant are listed in Table S 1. For the (alkyl)phenols, personal
234 care products, pesticides, pharmaceuticals, phthalates and steroidal EDCs, averaged class-specific
235 mass balances equaled 79±4%, 72±7%, 92±4%, 86±4, 82±2% and 75±4%, while averaged class-
236 specific repeatability was calculated to 5%, 11%, 4%, 8%, 2% and 5%, respectively. As
237 repeatabilities were well below 20%, it may be concluded that batch sorption experiments were
238 consistent and reproducible. Indeed, good to excellent mass balances were obtained for the
239 majority of compounds. Consequently, and because the applied analytical methods were optimised
240 and validated for aqueous matrices, it was decided to calculate the K_{sw} solely on water phase
241 concentrations. The remaining losses that were experienced to a certain extent for all compounds
242 were < 25% after 168h and may be assigned to adsorption to glass walls and/or hydrolysis as was
243 reported by Jeong et al. (2017) ³⁶ as well.

244 *Determination of the K_{sw} .* All organic contaminants studied in this work reached sorption
245 equilibrium between 12 and 24h. The calculated log transformed K_{sw} are listed for the individual

246 components in Table S 2, and are depicted per class of compounds in Figure 2. K_{sw} ranged over
247 more than 3 orders of magnitude, from $\log K_{sw}$ 4.00 for nalidixic acid (pharmaceutical) to 7.22 for
248 terbuthylazine (pesticide).

249 To the best of the author's knowledge, only one study of Jeong et al. (2017) determined the
250 sorption of 28 organic compounds to naked SPE sorbent (i.e. OasisTM HLB) in a static exposure
251 design. The $\log K_{sw}$ -values of specific compounds obtained in this study, i.e. metoprolol (5.65),
252 isoproturon (6.44), carbamazepine (6.44), flufenacetate (6.16), diuron (6.81), atrazine (6.33),
253 sulfamethoxazole (4.17), simazine (6.24) and terbutryn (6.42) are comparable (except for
254 sulfamethoxazole) or slightly higher ($\log K_{sw}$ -difference ranged between 0.41 and 1.55 log unit),
255 than those reported by Jeong et al. (2017) (5.15; 6.03; 5.64; 5.23; 5.26; 5.29; 4.44; 5.35 and 5.39,
256 respectively). These data suggest that the investigated polar compounds ($\log P < 4$) have a slightly
257 higher sorption tendency (higher K_{sw} values, availability of more divinylbenzene groups (see
258 characterization)) to hydrophilic DVB as compared to the OasisTM HLB sorbent. This agrees with
259 the functional characterization data, which demonstrated that hydrophilic DVB comprises
260 hydrophilic moieties with a higher polarity as does Oasis[®] HLB (see characterization), i.e.
261 carboxyl [-COOH] as opposed to N-vinylpyrrolidone groups.

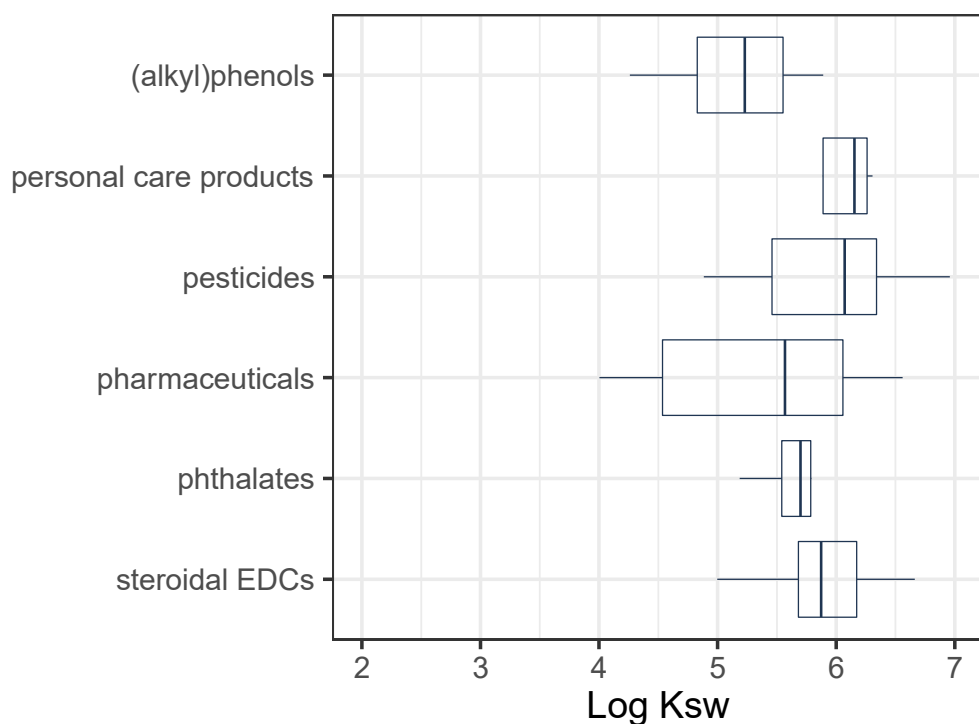
262 Comparing hydrophilic DVB to other SPE-based sampling devices (with sorbent casing) also
263 corroborates the conclusion that hydrophilic DVB covers a much broader polarity range ($\log P$
264 ranging from -1.30 to 9.85) than any previously tested sorbent. Ahrens et al. (2015) tested a broad
265 spectrum of organic compounds with $\log P$ values ranging from -1.7 to 6.9, and this for 5 different
266 polymer-based passive sampling devices, to conclude that the sorption of organic compounds to
267 each device was optimal within a specific polarity range. Silicone rubbers, Chemcatcher SDB-
268 RPS, Chemcatcher C18, POCIS A and POCIS B, effectively sampled organic compounds with \log

269 P values ranging respectively from 0.5 to 5.8, -1.3 to 4.0, 0.9 to 5.8, -1.6 to 5.5 and -1.6 to 5.5. O'
270 Connol et al. investigated silicone wristbands and found that 49 compounds were sequestered
271 during ambient deployment, encompassing a diverse set of compounds including polycyclic
272 aromatic hydrocarbons, consumer products, personal care products, pesticides, phthalates, and
273 other industrial compounds ranging in log K_{ow} from -0.07 (caffeine) to 9.49 (tris(2-ethylhexyl)
274 phosphate)³⁷. Since the above-mentioned study of Ahrens used different types of limiting
275 membranes, K_{sw} cannot be compared to our work. Comparing our results with the study of Ahrens
276 et al. (2015), also confirms that hydrophilic DVB is a more functionalised polymer and as such
277 enables the sorption of more hydrophobic compounds than OasisTM HLB.

278 In line with the ever-increasing number of chemicals that is released into the environment ¹,
279 several passive sampling-based studies have attempted to mathematically model log K_{sw} using
280 various physico-chemical properties of the compounds under investigation as input ^{7,38-40}. Up until
281 now, log P and molecular weight (MW) have been correlated frequently to the log K_{sw} ($r^2=0.92$,
282 $n=65$) ^{7,38,39} for more non-polar compounds ($\log P > 4$). However, using our complete dataset,
283 lack-of-fit (p -value < 0.05) between log P or MW and log K_{sw} was observed. Smedes et al. (2018)
284 observed similar findings for the PAHs (polycyclic aromatic hydrocarbons), PCBs
285 (polychlorinated biphenyls) and phthalates ⁴¹. Therefore, we evaluated the modelling potential of
286 a number of other physico-chemical properties, including V_x (molecular volume), qA^- (most
287 negative charge on O, N, S, X atoms), H_y (hydrophilic factor), vapor pressure, bioconcentration
288 factor, number of carbon atoms, pKa, water solubility and polar surface area. No valid model
289 ($R^2_{adj}=0.33$, $n=115$, all compounds for which described physico-chemical parameters were
290 available) was however obtained for predicting log K_{sw} with any of the above-mentioned
291 parameters or combinations thereof using the complete dataset. Additionally, it should be

292 highlighted that no quantitative effect of type and number of functional groups on the K_{sw} was
293 observed (see Figure S4). The above-mentioned results lead to conclude that the partitioning of
294 analytes towards hydrophilic DVB seems to be compound-specific and warrants individual
295 practical determination. The latter is exemplified by the observation that even enantiomers resulted
296 in different $\log K_{sw}$, i.e. 6.92 was observed for 17 α - while 5.39 was determined for 17 β -
297 testosterone. A similar phenomenon has also been observed during chromatographic separation of
298 analytes, demonstrating different affinities to stationary phases (resulting in different retention
299 times of e.g. testosterone, trenbolone, zearalenol and zeranol) ¹⁶.

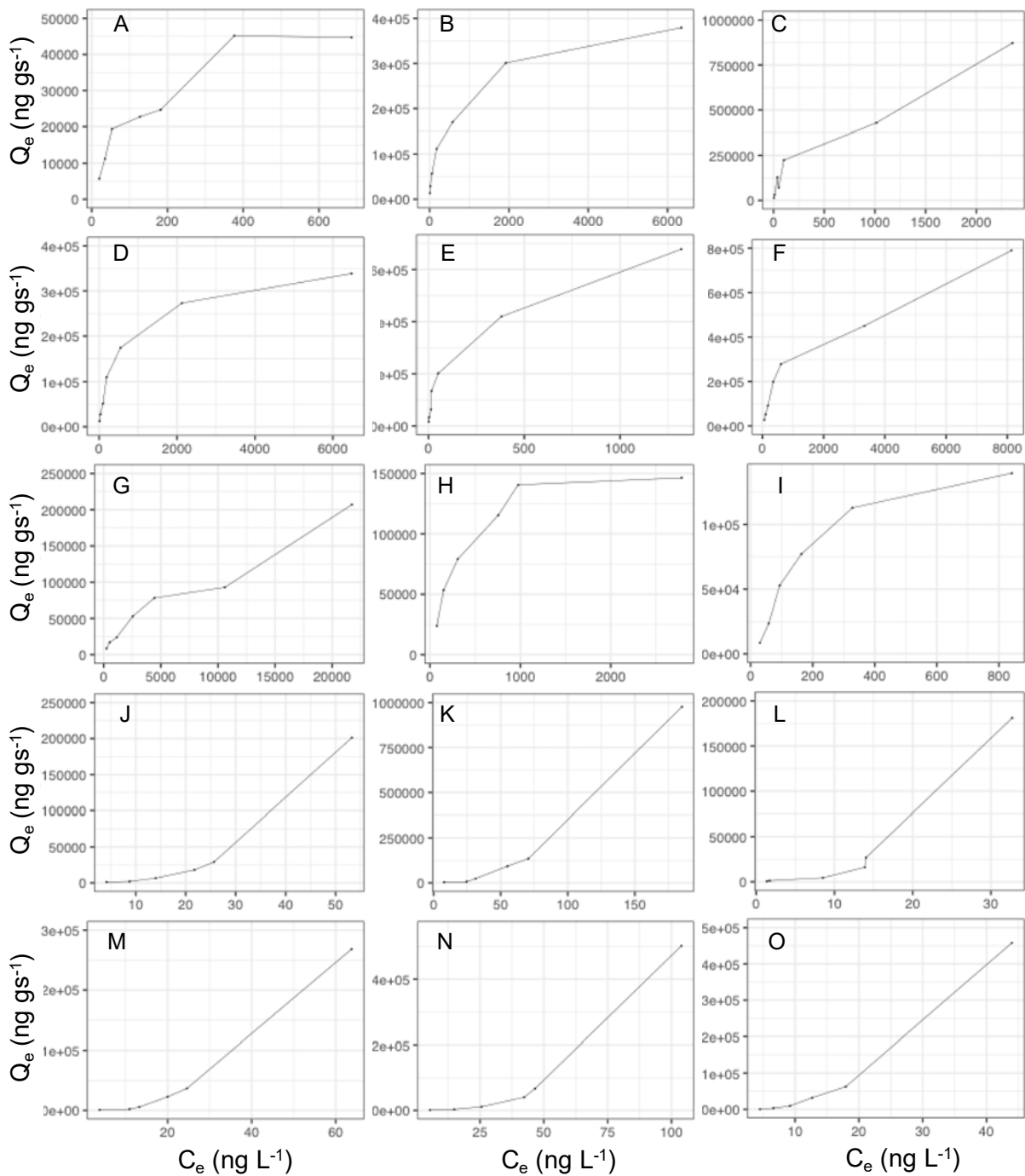
300



301
302 **Figure 2.** The calculated sorbent-water equilibrium partitioning coefficients ($\log K_{sw}$) of the
303 different classes, i.e. alkylphenols (n=4), personal care products (n=5), pesticides (n=25),
304 pharmaceuticals (n=32), phthalates (n=15) and steroidal EDCs (n=50). The batch systems were
305 kept at a constant temperature of 8°C, pH of 7 and salinity of 35 psu. We refer to SI Table 3 for

306 individual calculated sorbent-water equilibrium partitioning coefficients ($\log K_{sw}$) with
307 corresponding standard deviations (SD).

308
309 *Do increasing organic contaminant concentrations affect K_{sw} ?* The influence of dissolved
310 organic contaminant concentrations on their partitioning between artificial seawater and
311 hydrophilic DVB was investigated by varying compound concentrations while keeping the amount
312 of sorbent constant, as depicted for a selection of compounds in Figure 3. Changes in partitioning
313 and surface heterogeneity (reflected by the Freundlich exponent, n) were assessed by calculating
314 the K_{sw} (Eq. 1) and Freundlich isotherms (Eq. 2) respectively (Table S 3). For the steroidal EDCs,
315 higher dissolved concentrations resulted in increased K_{sw} ($n>1$), showing that higher initial
316 steroidal EDC concentrations tend to enhance sorption capacity. This phenomenon has also been
317 reported for methylene blue and phenol⁴²⁻⁴⁵, bearing a similar cyclic aromatic structure as do the
318 steroidal EDCs. For the (alkyl)phenols, personal care products, pesticides, pharmaceuticals and
319 phthalates, dissolved concentrations exceeding the linear ranges of the isotherms resulted for 95%
320 of the 131 studied compounds in reduced K_{sw} ($n<1$). The latter indicates that partitioning for these
321 groups of organic contaminant depends merely on the available hydrophilic DVB sorption sites.
322 The aforementioned findings stress the need to examine the linear range of the partitioning
323 isotherms for the different organic contaminants. For more than 75% of the steroidal EDCs ($n>1$)
324 and all the other classes of studied organic contaminants ($n<1$), linear isotherms were observed
325 when C_e was, respectively, lower than 8.5 ng L⁻¹ and 70 ng L⁻¹. The C_e -levels applied in our
326 experimental set-up are in the same order of magnitude than seawater concentrations recently
327 measured in the Belgian Part of the North Sea for the contaminants studied^{16,26,27}.



328

329 **Figure 3.** Partitioning isotherms ($T = 8^\circ\text{C}$) for a set of selected compounds representing the 6
 330 different classes, i.e. (alkyl)phenols: isopropylphenol (a), personal care products: methylparaben
 331 (b) and DEET (c), pesticides: acetamiprid (d) and diuron (e), pharmaceuticals: bezafibrate (f) and

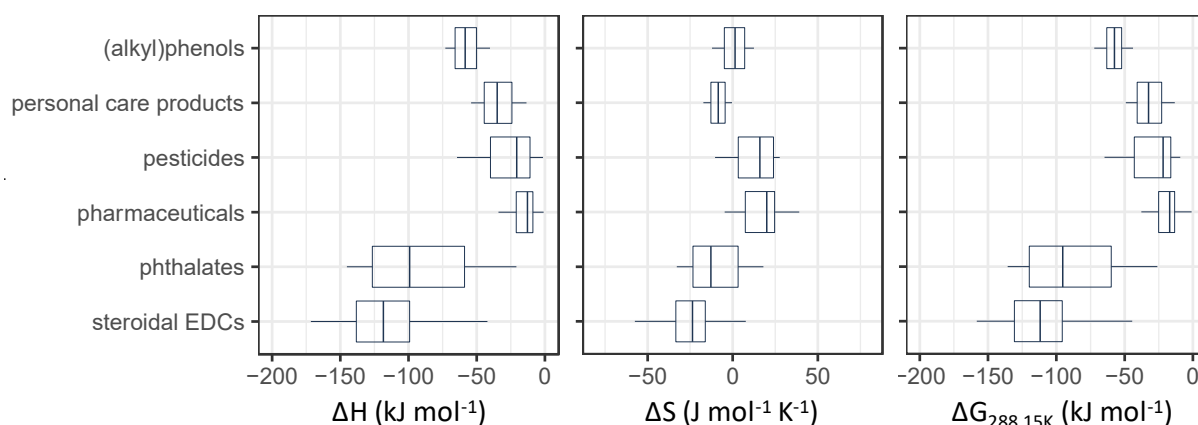
332 sarafloxacin (g), phthalates: monomethyl phthalate (h) and dimethyl phthalate (i), and steroidal
333 EDCs: 11 β -hydroxyandrosterone (j), estrone (k), norgestrel (l), 17 α -testosterone (m), 17 α -
334 acetoxyprogesterone (n) and β -zeranol (o).

335
336 *Do environmental conditions affect K_{sw} ?* The dependency of the K_{sw} on environmental
337 conditions was investigated using the Box-Behnken RSM design. Temperature, pH and salinity
338 each independently significantly ($p < 0.05$) impacted K_{sw} for most of the contaminants. Only for
339 the phthalates and alkylphenols (Tables S 4 and S 5), temperature did not significantly affect K_{sw} .
340 Overall, the effect of solely temperature on the K_{sw} was more significant as compared to pH and
341 salinity.

342 To better understand the nature of the partitioning process upon changing temperature, a number
343 of thermodynamic parameters (Figure 4 and Table S 6) were calculated using the van't Hoff
344 equation (Eq. 3) and the change in Gibbs free energy (Eq. 4). For all compounds (at fixed
345 conditions of pH and salinity), a decrease in log K_{sw} -values was observed (difference in log K_{sw}
346 ranged between 0.06 and 5.19), when increasing temperature with 12 $^{\circ}$ C (based on environmental
347 range) confirming the exothermic nature ($\Delta H < 0$) of the partitioning process.

348 The magnitude of ΔH may indicate the nature of the sorption process; i.e. between 0 and -40 kJ
349 mol $^{-1}$ for physisorption, whereas in case of chemisorption (covalent and ionic interactions) -400 kJ
350 mol $^{-1}$ will be mostly exceeded^{46,47}. It should be noted that there is no sharp boundary between
351 physisorption and chemisorption⁴⁸. The largest negative enthalpies were observed for the steroidal
352 EDCs ($\overline{\Delta H} = -113$ kJ mol $^{-1}$), followed by $\overline{\Delta H}_{phthalates} = -92$ kJ mol $^{-1}$, $\overline{\Delta H}_{alkylphenols} = -56$ kJ mol $^{-1}$,
353 $\overline{\Delta H}_{personal\ care\ products} = -32$ kJ mol $^{-1}$, $\overline{\Delta H}_{pesticides} = -25$ kJ mol $^{-1}$ and $\overline{\Delta H}_{pharmaceuticals} = -13$
354 kJ mol $^{-1}$. Physisorption indicates to be the main driver for partitioning of personal care products,

355 pesticides, pharmaceuticals and alkylphenols, and is dominated by Van der Waals interactions
 356 (weak interactions between compounds and sorbent that are sufficiently close to each other). The
 357 largest negative enthalpies were observed for the phthalates and steroidal EDCs. The sorption of
 358 phthalates and steroidal EDCs have shown to be driven by stronger interactions to the sorbent,
 359 such as hydrogen bonding. It can be presumed that partitioning of phthalates and steroidal EDCs
 360 is driven by multiple hydrogen bonding with the sorbent as the enthalpy change of an individual
 361 hydrogen bond amounts around 24 kJ mol^{-1} ⁴⁹. For those compounds for which partitioning is
 362 mainly dominated by physisorption and lack of strong interactions, the sorption process is more
 363 reversible. This could be useful to perform e.g. passive dosing experiments for toxicity testing ⁵⁰.
 364



365
 366 **Figure 4.** Thermodynamic parameters, i.e. change in enthalpy (ΔH), change in entropy (ΔS) and
 367 change in free Gibbs energy (ΔG) during sorption for the alkylphenols, personal care products,
 368 pesticides, pharmaceuticals, phthalates and steroidal EDCs.

369
 370 The steroidal EDCs also demonstrated a negative ΔS ($\overline{\Delta S}_{steroidal\ EDCs} = -23 \text{ J mol}^{-1} \text{ K}^{-1}$),
 371 suggesting no significant alteration of the molecular structure in the sorbed state ^{51,52}, which

372 implies that the sorption process is enthalpy-driven. For the other compound classes, less negative
373 ΔH and mainly positive ΔS values were observed. Vinmonses et al. (2009) suggested that positive
374 ΔS values mark structural changes taking place on the sorbent, and as such increase randomized
375 binding during sorption⁵³. The magnitude of the negative $\Delta G_{288.15K}$ value indicates the
376 spontaneous nature of the equilibrium sorption process, with higher negative values marking a
377 more spontaneous sorption to reach equilibrium at lower temperatures according to Ahmad and
378 Kumar (2010) and Vimonses et al. (2009). Our negative $\Delta G_{288.15K}$ data for the steroidal EDCs thus
379 indicate a more rapid, spontaneous and stronger bonding of the latter to the sorbent⁵³⁻⁵⁵, offering
380 an explanation for their relatively high $\log K_{sw}$ as compared to the other compound classes (Figure
381 2). Predicting the $\log K_{sw}$ based on the determined thermodynamic variables also resulted in a
382 lack-of-fit”.

383 With respect to the effect of pH, the $\log K_{sw}$ were not significantly ($p\text{-value} > 0.05$) impacted,
384 except for 11 out of 131 organic contaminants. No general conclusion can however be drawn with
385 relation to the impact of the pH on compound behaviour for all compound groups as the chemical
386 speciation of organic molecules in water is governed by both the aqueous pH and the compounds’
387 pKas. Similar results were reported by Stroski et al. (2018), with respect to the effect of pH on the
388 sorption of 28 out of 31 pesticides and pharmaceuticals⁵⁶. Only for strong cationic (rimantadine
389 and trimethoprim) and strong anionic compounds (i.e. sulfadoxine, sulfamethazine,
390 sulfamethoxazole and clorfibric acid), a pH dependency was noticed. Comparing the partitioning
391 at different pHs of sorbent and water, it was noted that an increased pH caused lower (difference
392 in $\log K_{sw}$ ranged between 0.24 and 0.82 over 3 pH-units) or higher (difference in $\log K_{sw}$ ranged
393 between 0.14 and 0.22 over 3 pH units) K_{sw} for cationic and anionic compounds, respectively.
394 These results are in line with the work of Jeong et al. (2017), which reported that pH tendency can

395 only be predicted for anionic and cationic compounds. In the current study, however, this was
396 merely observed for strong cationic and anionic compounds, more specifically mecoprop,
397 rimantadine, trimethoprim, venlafaxine, sulfadoxin, sulfamethazine, sulfamethoxazole and
398 clofibric acid.

399 Different salt concentrations were used to assess the influence of ionic strength on partitioning.
400 Altering the salinity did not impact (within the experimentally observed standard deviations of the
401 RSM) the K_{sw} of the steroidal EDCs, phthalates and (alkyl)phenols ($p > 0.05$). For the personal
402 care products, pesticides and pharmaceuticals, the influence of salinity on the K_{sw} was compound
403 specific (difference in $\log K_{sw}$ ranged between 0.01 and 1.16 over 35 psu units). These findings
404 agree well with previous work, in which it was demonstrated that the effect of salinity is
405 compound-specific^{24,57}. As salinity is known to impact the ionic composition of seawater, it may
406 be anticipated that the sorption process, which is pKa-dependent is affected by the salinity in a
407 compound-specific way. However, no significant relationship between the ionic strength and
408 compound-specific $\log K_{sw}$ value of the 131 selected organic contaminants was observed for any
409 of the sub-classes and the complete dataset.

410

411 ASSOCIATED CONTENT

412 Sorbent and water analysis

413 **Figures.** Figure S1: The particle size distribution of hydrophilic DVB. Figure S2. Schematic
414 overview of the sorbent and water analysis. During step 1 a glass fibre filter was used, in step 2
415 the most suitable cartridge (red colored) for each group of organic contaminants was used (see
416 specifications in table under the schematic overview). The yellow dots and yellow colored area
417 represent the hydrophilic DVB sorbent that was used in the experiments. Figure S3. The averaged

418 NIR spectra (n=3) of hydrophilic DVB (blue) and Oasis™ HLB(red). Figure S4. Chart depicting
419 the effect of type (y-axis) and number of functional groups (color intensity) on K_{sw} (x-axis).

420 **Tables.** Table S1. Descriptive table of the compounds used in the batch experiments. Group,
421 chemical formula, molecular weight and polarity are presented in the table. Table S2. The average
422 mass balance (%), standard deviation (SD) and the corresponding analytical repeatability (%
423 RSDs) of each organic contaminants studied. Table S3. The calculated sorbent-water equilibrium
424 partitioning coefficients (log K_{sw}) with their corresponding standard deviations (SD). n represents
425 the number of datapoints originating from time points after which equilibrium was established.
426 Log P represents the polarity index of the compound. Table S4. The calculated Freundlich
427 coefficients (KF) and exponents (n) with their corresponding standard deviation (SD) and
428 significance (p-value). The p-value represents the goodness-of-fit through the Freundlich model.
429 The Asterix(*) corresponds to compounds that could not be calculated, because concentrations
430 were detected below detection limits, resulting in in lack-of data points for constructing a
431 Freundlich model. Table S5. The statistical evaluation of the response surface modelling (RSM)
432 encompassing the significance of the interaction terms. The Asterix(*) corresponds to compounds
433 that could not be calculated, because concentrations were detected below detection limits, resulting
434 in in lack-of data points for constructing a reliable Box-Behnken design. T, pH and S corresponds
435 to temperature, acidity and salinity, respectively. Table S6. The coefficients of the obtained
436 response surface models. The Asterix(*) corresponds to compounds that could not be calculated,
437 because concentrations were detected below detection limits, resulting in in lack-of data points for
438 constructing a reliable Box-Behnken design. T, pH and S corresponds to temperature, acidity and
439 salinity, respectively. Table S7. The calculated thermodynamic parameters, i.e. change in enthalpy
440 ΔH (kJ/mol) , entropy ΔS (J/mol/K) and free Gibbs energy $\Delta G_{288.15K}$ (kJ/mol) (n=number of

441 available data-points during sorption for the calculations). The Asterix(*) corresponds to
442 compounds that could not be calculated, because concentrations were detected below detection
443 limits, resulting in in lack-of data points for constructing a reliable Box-Behnken design.

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447 **Author Contributions**

448 The manuscript was written through contributions of all authors. All authors have given approval
449 to the final version of the manuscript. ¹These first authors contributed equally. ²These senior
450 authors contributed equally.

451 **Funding Sources**

452 This work fits within the NewSTHEPS project (BR/143/A2/NEWTHEPS), supported by the
453 Belgian Science Policy (BELSPO). The contribution of Foppe Smedes was also supported by the
454 RECETOX Research Infrastructure (LM2015051 and CZ.02.1.01/0.0/0.0/16_013/0001761). The
455 financial support from the Hercules Foundation (Flemish Government; AUGÉ/11/016) and from
456 the Ghent University Special Research Fund (01B07512) is acknowledged for the UHPLC-Q-
457 Exactive™ and the automated SPE equipment, respectively.

458 ACKNOWLEDGMENT

459 The authors wish to thank prof. dr. Dumoulin Ann, M.Sc. Deprez Dieter and B.Sc.
460 Vandebussche Laura for their technical contribution to the manuscript.

461 ABBREVIATIONS

462 DVB, Hydrophilic divinylbenzene; SPE, solid-phase extraction; K_{sw}, sorbent-water partitioning
463 coefficients; PDMS, polydimethylsiloxane; SDB-RPS, sulfonated divinylbenzene - reversed
464 phase sulfonate; EDCs, endocrine disrupting compounds; RSM, response surface modelling;
465 FTIR, Fourier transform infrared; NIR, Near-infrared; MW, molecular weight; PAHs, polycyclic
466 aromatic hydrocarbons; PCBs, polychlorinated biphenyls.

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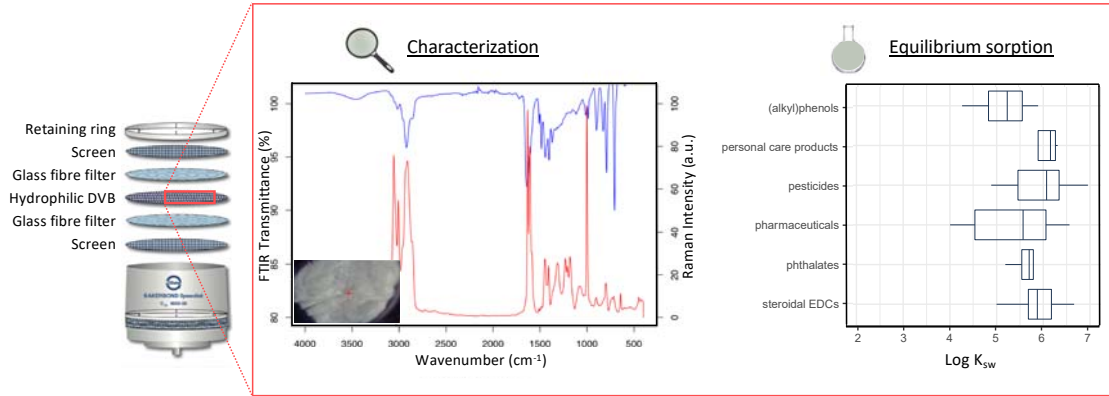
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659 SYNOPSIS (TOC)



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