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

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*. <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](#)

Publisher rights
Copyright 2019 ACS. This work is made available online in accordance with the publisher's policies. Please refer to any applicable terms of use of the publisher.

General rights
Copyright for the publications made accessible via the Queen's University Belfast Research Portal is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy
The Research Portal is Queen's institutional repository that provides access to Queen's research output. Every effort has been made to ensure that content in the Research Portal does not infringe any person's rights, or applicable UK laws. If you discover content in the Research Portal that you believe breaches copyright or violates any law, please contact openaccess@qub.ac.uk.

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

*Steve Huysman^{†,1}, Francis Vanryckeghem^{‡,1}, Ellen De Paepe[†], Foppe Smedes[§], Simon A.
Haughey^{||}, Christopher T. Elliott^{||}, Kristof Demeestere^{‡,2} and Lynn Vanhaecke^{*,†,||,2}*

[†] Ghent University, Faculty of Veterinary Medicine, Department of Veterinary Public Health and
Food Safety, Laboratory of Chemical Analysis (LCA), Merelbeke, Belgium;

[‡] Ghent University, Faculty of Bioscience Engineering, Department of Green Chemistry and
Technology, Research Group Environmental Organic Chemistry and Technology (EnVOC),
Ghent, Belgium;

[§] Masaryk University, Faculty of sciences, Research Centre for Toxic Compounds in the
Environment, Brno, Czech Republic;

^{||} Queen's University, Institute for Global Food Security, School of Biological Sciences, Belfast,
Northern Ireland.

KEYWORDS

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

ABSTRACT

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

INTRODUCTION

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

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

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

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

MATERIALS AND METHODS

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

USA), Lipomed GmbH (Germany), MpBio (Belgium) and TRC (Canada), covering 6 major classes, i.e. 4 alkylphenols, 5 personal care products, 25 pesticides, 32 pharmaceuticals, 15 phthalates and 50 steroidal endocrine disrupting compounds (EDCs). The selected organic contaminants were based on legislative frameworks and directives for protecting surface and marine waters, i.e. the U.S. Clean Water Act, the EU WFD watchlist, OSPAR, Reach and Norman^{18–22}. Primary stock solutions and standard mixtures were prepared in pure methanol (CH₃OH) or in a mixture of methanol/water (10/90, v/v %) with 0.1% (v/v %) formic acid and 0.1 g L⁻¹ Na₂EDTA.2H₂O, the latter only for pesticides, pharmaceuticals and personal care products, thereby attaining concentrations between 0.01 and 1000 ng µL⁻¹. Solutions were stored in dark glass bottles at -20°C. Organic solvents were of Optima UPLC-MS grade, purchased from Fisher Scientific (Loughborough, UK). The inorganic salts, used to prepare reference seawater, were supplied by Sigma Aldrich (St. Louis, MO, USA) and processed according to ASTM D-1141²³. The hydrophilic divinylbenzene (DVB) Speedisks® and Oasis® HLB cartridges (200 and 500 mg) were purchased from Filterservice (Eupen, Belgium) and Waters (Brussels, Belgium), respectively.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$\Delta G_{288.15K} = \Delta H^\circ - T\Delta S^\circ \quad (4)$$

RESULTS AND DISCUSSION

Sorbent characterization. To the best of our knowledge, the surface chemistry of hydrophilic DVB has not been studied earlier. This work relied on spectral analysis (i.e. FTIR, Raman and NIR) to unravel surface functionalities of hydrophilic DVB. Additionally, the co-polymer poly(divinylbenzene-co-N-vinylpyrrolidone), also more familiar under the tradename Oasis[®] HLB, was analysed for comparison. FTIR and Raman spectra are presented in Figure 1, whilst 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 , $R^2(X)(\text{cum}) = 0.989$, $R^2(Y) = 0.99$, $Q^2(\text{cum})$
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

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

Equilibrium partitioning between water and hydrophilic DVB. Mass balances. The applied analytical methods for the quantification of the 131 organic contaminants studied in this work, have been extensively and successfully validated as reported earlier^{16,26,27}. To assure that decreasing contaminant concentrations measured in the aqueous phase during the aforementioned batch tests were merely caused by sorption on the sorbent, mass balances were calculated for every contaminant. This was achieved by comparing the initially spiked contaminant quantity to the sum of the fractions remaining in the water and sorbent phases³⁵. Average mass balances (%) and corresponding analytical repeatabilities (% RSD) of the different time points in equilibrium (constant K_{sw}) for each studied contaminant are listed in Table S 1. For the (alkyl)phenols, personal care products, pesticides, pharmaceuticals, phthalates and steroidal EDCs, averaged class-specific mass balances equaled 79±4%, 72±7%, 92±4%, 86±4, 82±2% and 75±4%, while averaged class-specific repeatability was calculated to 5%, 11%, 4%, 8%, 2% and 5%, respectively. As repeatabilities were well below 20%, it may be concluded that batch sorption experiments were consistent and reproducible. Indeed, good to excellent mass balances were obtained for the majority of compounds. Consequently, and because the applied analytical methods were optimised and validated for aqueous matrices, it was decided to calculate the K_{sw} solely on water phase concentrations. The remaining losses that were experienced to a certain extent for all compounds were < 25% after 168h and may be assigned to adsorption to glass walls and/or hydrolysis as was reported by Jeong et al. (2017)³⁶ as well.

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

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

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

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

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

In line with the ever-increasing number of chemicals that is released into the environment¹, several passive sampling-based studies have attempted to mathematically model log K_{sw} using various physico-chemical properties of the compounds under investigation as input^{7,38-40}. Up until now, log P and molecular weight (MW) have been correlated frequently to the log K_{sw} ($r^2=0.92$, $n=65$)^{7,38,39} for more non-polar compounds ($\log P > 4$). However, using our complete dataset, lack-of-fit ($p\text{-value} < 0.05$) between log P or MW and log K_{sw} was observed. Smedes et al. (2018) observed similar findings for the PAHs (polycyclic aromatic hydrocarbons), PCBs (polychlorinated biphenyls) and phthalates⁴¹. Therefore, we evaluated the modelling potential of a number of other physico-chemical properties, including V_x (molecular volume), qA^- (most negative charge on O, N, S, X atoms), H_y (hydrophilic factor), vapor pressure, bioconcentration factor, number of carbon atoms, pKa, water solubility and polar surface area. No valid model ($R^2_{adj}=0.33$, $n=115$, all compounds for which described physico-chemical parameters were available) was however obtained for predicting log K_{sw} with any of the above-mentioned parameters or combinations thereof using the complete dataset. Additionally, it should be

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

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

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

Do increasing organic contaminant concentrations affect K_{sw} ? The influence of dissolved organic contaminant concentrations on their partitioning between artificial seawater and hydrophilic DVB was investigated by varying compound concentrations while keeping the amount of sorbent constant, as depicted for a selection of compounds in Figure 3. Changes in partitioning and surface heterogeneity (reflected by the Freundlich exponent, n) were assessed by calculating the K_{sw} (Eq. 1) and Freundlich isotherms (Eq. 2) respectively (Table S 3). For the steroidal EDCs, higher dissolved concentrations resulted in increased K_{sw} ($n > 1$), showing that higher initial steroidal EDC concentrations tend to enhance sorption capacity. This phenomenon has also been reported for methylene blue and phenol^{42–45}, bearing a similar cyclic aromatic structure as do the steroidal EDCs. For the (alkyl)phenols, personal care products, pesticides, pharmaceuticals and phthalates, dissolved concentrations exceeding the linear ranges of the isotherms resulted for 95% of the 131 studied compounds in reduced K_{sw} ($n < 1$). The latter indicates that partitioning for these groups of organic contaminant depends merely on the available hydrophilic DVB sorption sites. The aforementioned findings stress the need to examine the linear range of the partitioning isotherms for the different organic contaminants. For more than 75% of the steroidal EDCs ($n > 1$) and all the other classes of studied organic contaminants ($n < 1$), linear isotherms were observed when C_e was, respectively, lower than 8.5 ng L⁻¹ and 70 ng L⁻¹. The C_e -levels applied in our experimental set-up are in the same order of magnitude than seawater concentrations recently measured in the Belgian Part of the North Sea for the contaminants studied^{16,26,27}.

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

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

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

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

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

pesticides, pharmaceuticals and alkylphenols, and is dominated by Van der Waals interactions (weak interactions between compounds and sorbent that are sufficiently close to each other). The largest negative enthalpies were observed for the phthalates and steroidal EDCs. The sorption of phthalates and steroidal EDCs have shown to be driven by stronger interactions to the sorbent, such as hydrogen bonding. It can be presumed that partitioning of phthalates and steroidal EDCs is driven by multiple hydrogen bonding with the sorbent as the enthalpy change of an individual hydrogen bond amounts around 24 kJ mol^{-1} ⁴⁹. For those compounds for which partitioning is mainly dominated by physisorption and lack of strong interactions, the sorption process is more reversible. This could be useful to perform e.g. passive dosing experiments for toxicity testing⁵⁰.

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

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

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

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

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

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

ASSOCIATED CONTENT

Sorbent and water analysis

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

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

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

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

AUTHOR INFORMATION

Corresponding Author

* Tel: +32 9 264 74 75. E-mail: Lynn.Vanhaecke@UGent.be

Author Contributions

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

Funding Sources

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

ACKNOWLEDGMENT

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

ABBREVIATIONS

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

REFERENCES

- (1) Scheringer, M. Environmental Chemistry and Ecotoxicology: In Greater Demand than Ever. *Environmental Sciences Europe*. 2017, p 3. <https://doi.org/10.1186/s12302-016-0101-x>.
- (2) Andrade-Eiroa, A.; Canle, M.; Leroy-Cancellieri, V.; Cerdà, V. Solid-Phase Extraction of Organic Compounds: A Critical Review (Part I). *TrAC - Trends in Analytical Chemistry*. Elsevier June 1, 2016, pp 641–654. <https://doi.org/10.1016/j.trac.2015.08.015>.
- (3) Asgarpour Khansary, M.; Shirazian, S.; Asadollahzadeh, M. Polymer-Water Partition Coefficients in Polymeric Passive Samplers. *Environ. Sci. Pollut. Res.* **2017**, 24 (3), 2627–2631. <https://doi.org/10.1007/s11356-016-8029-7>.
- (4) Thompson, J. M.; Hsieh, C. H.; Luthy, R. G. Modeling Uptake of Hydrophobic Organic Contaminants into Polyethylene Passive Samplers. *Environ. Sci. Technol.* **2015**, 49 (4), 2270–2277. <https://doi.org/10.1021/es504442s>.
- (5) Ahrens, L.; Daneshvar, A.; Lau, A. E.; Kreuger, J. Characterization of Five Passive Sampling Devices for Monitoring of Pesticides in Water. *J. Chromatogr. A* **2015**, 1405, 1–11. <https://doi.org/10.1016/j.chroma.2015.05.044>.

- 483 (6) Martin, A.; Margoum, C.; Randon, J.; Coquery, M. Silicone Rubber Selection for Passive
484 Sampling of Pesticides in Water. *Talanta* **2016**, *160*, 306–313.
485 <https://doi.org/10.1016/j.talanta.2016.07.019>.
- 486 (7) Smedes, F.; Geertsma, R. W.; Van Der Zande, T.; Booij, K. Polymer-Water Partition
487 Coefficients of Hydrophobic Compounds for Passive Sampling: Application of Cosolvent
488 Models for Validation. *Environ. Sci. Technol.* **2009**, *43* (18), 7047–7054.
489 <https://doi.org/10.1021/es9009376>.
- 490 (8) Lissalde, S.; Charriau, A.; Poulier, G.; Mazzella, N.; Buzier, R.; Guibaud, G. Overview of
491 the Chemcatcher® for the Passive Sampling of Various Pollutants in Aquatic Environments
492 Part B: Field Handling and Environmental Applications for the Monitoring of Pollutants
493 and Their Biological Effects. *Talanta*. Elsevier February 1, 2016, pp 572–582.
494 <https://doi.org/10.1016/j.talanta.2015.06.076>.
- 495 (9) Charriau, A.; Lissalde, S.; Poulier, G.; Mazzella, N.; Buzier, R.; Guibaud, G. Overview of
496 the Chemcatcher® for the Passive Sampling of Various Pollutants in Aquatic Environments
497 Part A: Principles, Calibration, Preparation and Analysis of the Sampler. *Talanta* **2016**, *148*,
498 556–571. <https://doi.org/10.1016/J.TALANTA.2015.06.064>.
- 499 (10) Booij, K.; Chen, S. Review of Atrazine Sampling by Polar Organic Chemical Integrative
500 Samplers and Chemcatcher. *Environ. Toxicol. Chem.* **2018**, *37* (7), 1786–1798.
501 <https://doi.org/10.1002/etc.4160>.
- 502 (11) Alvarez, D. a; Petty, J. D.; Huckins, J. N.; Jones-Lepp, T. L.; Getting, D. T.; Goddard, J. P.;
503 Manahan, S. E. Development of a Passive, in Situ, Integrative Sampler for Hydrophilic
504 Organic Contaminants in Aquatic Environments. *Environ. Toxicol. Chem.* **2004**, *23* (7),

- 505 1640–1648. <https://doi.org/10.1897/03-603>.
- 506 (12) Metcalfe, C.; Hoque, M. E.; Sultana, T.; Murray, C.; Helm, P.; Kleywegt, S. Monitoring for
507 Contaminants of Emerging Concern in Drinking Water Using POCIS Passive Samplers.
508 *Environ. Sci. Process. Impacts* **2014**, *16* (3), 473. <https://doi.org/10.1039/c3em00508a>.
- 509 (13) Stiles, R.; Yang, I.; Lippincott, R. L.; Murphy, E.; Buckley, B. Measurement of Drinking
510 Water Contaminants by Solid Phase Microextraction Initially Quantified in Source Water
511 Samples by the USGS. *Environ. Sci. Technol.* **2008**, *42* (8), 2976–2981.
512 <https://doi.org/10.1021/es071804i>.
- 513 (14) Kermani, F. R.; Tugulea, A.-M.; Hnatiw, J.; Niri, V. H.; Pawliszyn, J. Application of
514 Automated Solid-Phase Microextraction to Determine Haloacetonitriles, Haloketones, and
515 Chloropicrin in Canadian Drinking Water. *Water Qual. Res. J.* **2013**, *48* (1), 85–98.
516 <https://doi.org/10.2166/wqrjc.2013.012>.
- 517 (15) Grandy, J. J.; Singh, V.; Lashgari, M.; Gauthier, M.; Pawliszyn, J. Development of a
518 Hydrophilic Lipophilic Balanced Thin Film Solid Phase Microextraction Device for
519 Balanced Determination of Volatile Organic Compounds. *Anal. Chem.* **2018**, *90* (23),
520 14072–14080. <https://doi.org/10.1021/acs.analchem.8b04544>.
- 521 (16) Huysman, S.; Van Meulebroek, L.; Vanryckeghem, F.; Van Langenhove, H.; Demeestere,
522 K.; Vanhaecke, L. Development and Validation of an Ultra-High Performance Liquid
523 Chromatographic High Resolution Q-Orbitrap Mass Spectrometric Method for the
524 Simultaneous Determination of Steroidal Endocrine Disrupting Compounds in Aquatic
525 Matrices. *Anal. Chim. Acta* **2017**, *984*. <https://doi.org/10.1016/j.aca.2017.07.001>.

- 526 (17) Fontanals, N.; Marcé, R. M.; Borrull, F. Overview of the Novel Sorbents Available in Solid-
527 Phase Extraction to Improve the Capacity and Selectivity of Analytical Determinations.
528 *Contrib. to Sci.* **2011**, 6 (2), 199–213. <https://doi.org/10.2436/20.7010.01.97>.
- 529 (18) European Commission. *Commission Implementing Decision (EU) 2015/495 of 20 March*
530 *2015 Establishing a Watch List of Substances for Union-Wide Monitoring in the Field of*
531 *Water Policy Pursuant to Directive 2008/105/EC of the European Parliament and of the*
532 *Council*; 2015; Vol. 58, pp 40–42. [https://doi.org/http://eur-](https://doi.org/http://eur-lex.europa.eu/pri/en/oj/dat/2003/l_285/l_28520031101en00330037.pdf)
533 [lex.europa.eu/pri/en/oj/dat/2003/l_285/l_28520031101en00330037.pdf](https://doi.org/http://eur-lex.europa.eu/pri/en/oj/dat/2003/l_285/l_28520031101en00330037.pdf).
- 534 (19) Slobodnik, N. A. *NORMAN Position Paper Collection, Exchange and Interpretation of*
535 *Data on Emerging Substances Towards a Harmonised Approach for Collection and*
536 *Interpretation of Data on Emerging Substances in Support of European Environmental*
537 *Policies*; 2014.
- 538 (20) Ospar. OSPAR Commission <https://www.ospar.org/about/publications> (accessed Dec 4,
539 2018).
- 540 (21) European Chemicals Agency. Understanding Reach
541 [https://echa.europa.eu/regulations/reach/understanding-](https://echa.europa.eu/regulations/reach/understanding-reach%5Cnhttp://echa.europa.eu/web/guest/regulations/reach/understanding-reach)
542 [reach%5Cnhttp://echa.europa.eu/web/guest/regulations/reach/understanding-reach](http://echa.europa.eu/web/guest/regulations/reach/understanding-reach).
- 543 (22) Copeland, C. Clean Water Act: A Summary of the Law. In *Atmospheric Deposition of*
544 *Pollutants and the EPA*; 2012. <https://doi.org/10.4172/2332-0915.1000133>.
- 545 (23) International, A. *ASTM D-1141-98(2013) Seawater*; 2013.
- 546 (24) Bayen, S.; Segovia, E.; Loh, L. L.; Burger, D. F.; Eikaas, H. S.; Kelly, B. C. Application of

- 547 Polar Organic Chemical Integrative Sampler (POCIS) to Monitor Emerging Contaminants
548 in Tropical Waters. *Sci. Total Environ.* **2014**, 482–483 (1), 15–22.
549 <https://doi.org/10.1016/j.scitotenv.2014.02.082>.
- 550 (25) MacLeod, S. L.; McClure, E. L.; Wong, C. S. Laboratory Calibration and Field Deployment
551 of the Polar Organic Chemical Integrative Sampler for Pharmaceuticals and Personal Care
552 Products in Wastewater and Surface Water. *Environ. Toxicol. Chem.* **2007**, 26 (12), 2517–
553 2529. <https://doi.org/10.1897/07-238.1>.
- 554 (26) Huysman, S.; Van Meulebroek, L.; Janssens, O.; Vanryckeghem, F.; Van Langenhove, H.;
555 Demeestere, K.; Vanhaecke, L. Targeted Quantification and Untargeted Screening of
556 Alkylphenols, Bisphenol A and Phthalates in Aquatic Matrices Using Ultra-High-
557 Performance Liquid Chromatography Coupled to Hybrid Q-Orbitrap Mass Spectrometry.
558 *Anal. Chim. Acta* **2019**, 1049, 141–151. <https://doi.org/10.1016/j.aca.2018.10.045>.
- 559 (27) Vanryckeghem, F.; Huysman, S.; Van Langenhove, H.; Vanhaecke, L.; Demeestere, K.
560 Multi-Residue Quantification and Screening of Emerging Organic Micropollutants in the
561 Belgian Part of the North Sea by Use of Speedisk Extraction and Q-Orbitrap HRMS
562 (Submitted). *Mar. Pollut. Bull.* **2019**.
- 563 (28) Harman, C.; Allan, I. J.; Vermeirssen, E. L. M. Calibration and Use of the Polar Organic
564 Chemical Integrative Sampler-a Critical Review. *Environ. Toxicol. Chem.* **2012**, 31 (12),
565 2724–2738. <https://doi.org/10.1002/etc.2011>.
- 566 (29) Tran, H. N.; You, S. J.; Hosseini-Bandegharai, A.; Chao, H. P. Mistakes and
567 Inconsistencies Regarding Adsorption of Contaminants from Aqueous Solutions: A Critical
568 Review. *Water Research*. Pergamon September 1, 2017, pp 88–116.

- 569 <https://doi.org/10.1016/j.watres.2017.04.014>.
- 570 (30) Kizil, R.; Irudayaraj, J.; Seetharaman, K. Characterization of Irradiated Starches by Using
571 FT-Raman and FTIR Spectroscopy. *J. Agric. Food Chem.* **2002**, *50* (14), 3912–3918.
572 <https://doi.org/10.1021/jf011652p>.
- 573 (31) Guo, X.; Liu, L.; Wu, J.; Fan, J.; Wu, Y. Qualitatively and Quantitatively Characterizing
574 Water Adsorption of a Cellulose Nanofiber Film Using Micro-FTIR Spectroscopy. *RSC*
575 *Adv.* **2018**, *8* (8), 4214–4220. <https://doi.org/10.1039/c7ra09894d>.
- 576 (32) Mizuguchi, M.; Nara, M.; Kawano, K.; Nitta, K. FT-XR Study of the Ca²⁺-Binding to
577 Bovine α -Lactalbumin. Relationships between the Type of Coordination and Characteristics
578 of the Bands Due to the Asp COO-Groups in the Ca²⁺-Binding Site. *FEBS Lett.* **1997**, *417*
579 (1), 153–156. [https://doi.org/10.1016/S0014-5793\(97\)01274-X](https://doi.org/10.1016/S0014-5793(97)01274-X).
- 580 (33) Taguchi, Y.; Noguchi, T. Drastic Changes in the Ligand Structure of the Oxygen-Evolving
581 Mn Cluster upon Ca²⁺ Depletion as Revealed by FTIR Difference Spectroscopy. *Biochim.*
582 *Biophys. Acta - Bioenerg.* **2007**, *1767* (6), 535–540.
583 <https://doi.org/10.1016/j.bbabi.2006.11.002>.
- 584 (34) Davidson, B.; Murray, A. A.; Elfick, A.; Spears, N. Raman Micro-Spectroscopy Can Be
585 Used to Investigate the Developmental Stage of the Mouse Oocyte. *PLoS One* **2013**, *8* (7),
586 e67972. <https://doi.org/10.1371/journal.pone.0067972>.
- 587 (35) Jeong, Y.; Schäffer, A.; Smith, K. Comparison of the Sampling Rates and Partitioning
588 Behaviour of Polar and Non-Polar Contaminants in the Polar Organic Chemical Integrative
589 Sampler and a Monophasic Mixed Polymer Sampler for Application as an Equilibrium

- 590 Passive Sampler. *Sci. Total Environ.* **2018**, 627, 905–915.
 591 <https://doi.org/10.1016/j.scitotenv.2018.01.273>.
- 592 (36) Jeong, Y.; Schäffer, A.; Smith, K. Equilibrium Partitioning of Organic Compounds to
 593 OASIS HLB, as a Function of Compound Concentration, PH, Temperature and Salinity.
 594 *Chemosphere* **2017**, 174, 297–305. <https://doi.org/10.1016/j.chemosphere.2017.01.116>.
- 595 (37) O’Connell, S. G.; Kincl, L. D.; Anderson, K. A. Silicone Wristbands as Personal Passive
 596 Samplers. *Environ. Sci. Technol.* **2014**, 48 (6), 3327–3335.
 597 <https://doi.org/10.1021/es405022f>.
- 598 (38) Lohmann, R. Critical Review of Low-Density Polyethylene’s Partitioning and Diffusion
 599 Coefficients for Trace Organic Contaminants and Implications for Its Use as a Passive
 600 Sampler. *Environ. Sci. Technol.* **2012**, 46 (2), 606–618. <https://doi.org/10.1021/es202702y>.
- 601 (39) Choi, Y.; Cho, Y. M.; Luthy, R. G. Polyethylene-Water Partitioning Coefficients for Parent-
 602 and Alkylated-Polycyclic Aromatic Hydrocarbons and Polychlorinated Biphenyls. *Environ.*
 603 *Sci. Technol.* **2013**, 47 (13), 6943–6950. <https://doi.org/10.1021/es304566v>.
- 604 (40) Liu, H.; Wei, M.; Yang, X.; Yin, C.; He, X. Development of TLSE Model and QSAR
 605 Model for Predicting Partition Coefficients of Hydrophobic Organic Chemicals between
 606 Low Density Polyethylene Film and Water. *Sci. Total Environ.* **2017**, 574, 1371–1378.
 607 <https://doi.org/10.1016/J.SCITOTENV.2016.08.051>.
- 608 (41) Smedes, F. Silicone–Water Partition Coefficients Determined by Cosolvent Method for
 609 Chlorinated Pesticides, Musks, Organo Phosphates, Phthalates and More. *Chemosphere*
 610 **2018**, 210, 662–671. <https://doi.org/10.1016/j.chemosphere.2018.07.054>.

- 611 (42) Ovchinnikov, O. V.; Evtukhova, A. V.; Kondratenko, T. S.; Smirnov, M. S.; Khokhlov, V.
 612 Y.; Erina, O. V. Manifestation of Intermolecular Interactions in FTIR Spectra of Methylene
 613 Blue Molecules. *Vib. Spectrosc.* **2016**, *86*, 181–189.
 614 <https://doi.org/10.1016/J.VIBSPEC.2016.06.016>.
- 615 (43) Abdelwahab, O.; Amin, N. K. Adsorption of Phenol from Aqueous Solutions by Luffa
 616 Cylindrica Fibers: Kinetics, Isotherm and Thermodynamic Studies. *Egypt. J. Aquat. Res.*
 617 **2013**, *39* (4), 215–223. <https://doi.org/10.1016/j.ejar.2013.12.011>.
- 618 (44) Ocampo-Perez, R.; Leyva-Ramos, R.; Mendoza-Barron, J.; Guerrero-Coronado, R. M.
 619 Adsorption Rate of Phenol from Aqueous Solution onto Organobentonite: Surface
 620 Diffusion and Kinetic Models. *J. Colloid Interface Sci.* **2011**, *364* (1), 195–204.
 621 <https://doi.org/10.1016/j.jcis.2011.08.032>.
- 622 (45) Lü, G.; Hao, J.; Liu, L.; Ma, H.; Fang, Q.; Wu, L.; Wei, M.; Zhang, Y. The Adsorption of
 623 Phenol by Lignite Activated Carbon. *Chinese J. Chem. Eng.* **2011**, *19* (3), 380–385.
 624 [https://doi.org/10.1016/S1004-9541\(09\)60224-X](https://doi.org/10.1016/S1004-9541(09)60224-X).
- 625 (46) Ahlert, R. C. Process Dynamics in Environmental Systems. *Environ. Prog.* **1997**, *16* (1),
 626 S6–S7. <https://doi.org/10.1002/ep.3300160107>.
- 627 (47) Leuenberger, M. C.; Schibig, M. F.; Nyfeler, P. Gas Adsorption and Desorption Effects on
 628 Cylinders and Their Importance for Long-Term Gas Records. *Atmos. Meas. Tech.* **2015**, *8*
 629 (12), 5289–5299. <https://doi.org/10.5194/amt-8-5289-2015>.
- 630 (48) Adamson, A. W. Physical Chemistry of Surfaces. *J. Electrochem. Soc.* **1977**, *124* (5), 192C.
 631 <https://doi.org/10.1149/1.2133374>.

- 632 (49) Robin, G. *Chemical Fundamentals of Geology and Environmental Geoscience*; 2015.
633 <https://doi.org/10.1017/CBO9781107415324.004>.
- 634 (50) Vorkamp, K.; McGeer, J. C. How to Improve Exposure Assessment. In *Aquatic*
635 *Ecotoxicology: Advancing Tools for Dealing with Emerging Risks*; Academic Press, 2015;
636 pp 77–102. <https://doi.org/10.1016/B978-0-12-800949-9.00004-8>.
- 637 (51) Tejraj, M.; Shivaputrappa, B. Kinetic and Thermodynamic Study on the Sorption of Liquids
638 by Polymer Films: A Simple Laboratory Experiment. **1991**, 68 (4), 343–346.
639 <https://doi.org/10.1021/ed068p343>.
- 640 (52) Sujana, M. G.; Pradhan, H. K.; Anand, S. Studies on Sorption of Some Geomaterials for
641 Fluoride Removal from Aqueous Solutions. *J. Hazard. Mater.* **2009**, 161 (1), 120–125.
642 <https://doi.org/10.1016/j.jhazmat.2008.03.062>.
- 643 (53) Vimonses, V.; Lei, S.; Jin, B.; Chow, C. W. K.; Saint, C. Kinetic Study and Equilibrium
644 Isotherm Analysis of Congo Red Adsorption by Clay Materials. *Chem. Eng. J.* **2009**, 148
645 (2–3), 354–364. <https://doi.org/10.1016/j.cej.2008.09.009>.
- 646 (54) Kebede, S. *Groundwater in Ethiopia: Features, Numbers and Opportunities*; 2013; Vol.
647 162. <https://doi.org/10.1007/978-3-642-30391-3>.
- 648 (55) Ahmad, R.; Kumar, R. Adsorptive Removal of Congo Red Dye from Aqueous Solution
649 Using Bael Shell Carbon. *Appl. Surf. Sci.* **2010**, 257 (5), 1628–1633.
650 <https://doi.org/10.1016/j.apsusc.2010.08.111>.
- 651 (56) Stroski, K. M.; Challis, J. K.; Wong, C. S. The Influence of PH on Sampler Uptake for an
652 Improved Configuration of the Organic-Diffusive Gradients in Thin Films Passive Sampler.

653 *Anal. Chim. Acta* **2018**, *1018*, 45–53. <https://doi.org/10.1016/j.aca.2018.02.074>.

654 (57) Zhang, Z.; Hibberd, A.; Zhou, J. L. Analysis of Emerging Contaminants in Sewage Effluent
655 and River Water: Comparison between Spot and Passive Sampling. *Anal. Chim. Acta* **2008**,
656 *607* (1), 37–44. <https://doi.org/10.1016/j.aca.2007.11.024>.

657

658