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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. 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. 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. 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. However, most studies focus on specific polymeric passive samplers efficiently binding compounds within a specific polarity range. 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), 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. In this context, the Oasis HLB® co-polymer has gained in popularity and was recently incorporated in different POCIS configurations, as it permits the accumulation of very polar to moderately non-polar compounds (log P ranging from -1.6 up to 5). Its affinity towards hydrophobic compounds (log P > 5) however still remains a hurdle. 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, 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®. 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 DVB. 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 Ksw 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 Ksw. 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-1141 23. 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 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 S2). 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 \cite{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 (R² > 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 ($N_w; \text{nmol}$) phase at start conditions ($t=0$) and equilibrium ($t=\text{equilibrium}$), concentration measured in the water phase at equilibrium ($C_{w,t=\text{equilibrium}}; \text{nmol L}^{-1}$) and the amount of sorbent ($M_s; \text{kg}$). \cite{28}
Adsorption modelling. Adsorption isotherms were investigated by applying the Freundlich model (see Eq. 2), 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 parameters, i.e. change in Gibbs free energy (\( \Delta G_{298,15K} \)), enthalpy (\( \Delta H \)) and entropy (\( \Delta S \)), 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).

\[
q_e = K_F C_e^n
\]  
(2)

\[
\ln(K^o) = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R}
\]  
(3)

\[
\Delta G_{298.15K} = \Delta H^o - T\Delta S^o
\]  
(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.
Figure 1. Averaged FTIR (A, n = 3 for each sorbent) and Raman (B, n = 3 for each sorbent) spectroscopic analysis of hydrophilic DVB (Bakerbond™) (Blue) and Oasis® HLB (red).
Multivariate statistical analysis of the obtained FTIR spectra demonstrated significant differences between the two sorbents (p-value < 0.05, R²(X)(cum) = 0.989, R²(Y) = 0.99, Q²(cum) = 0.974). The main spectral differences consisted of FTIR peaks at 1642 and 1403 cm⁻¹ for hydrophilic DVB, and 1684 cm⁻¹ for Oasis® HLB. An FTIR peak at 1642 cm⁻¹ has been related to the presence of water adsorbed to amorphous regions of a polymer [30,31], suggesting the presence of hydroxyl [-OH] and/or ketone [-C=O] groups. The FTIR peak at 1403 cm⁻¹ of hydrophilic DVB represents the presence of carboxyl [-COOH] groups [32,33]. For Oasis® HLB, the FTIR peak at 1684 cm⁻¹ corresponds to the amide [C-N] stretching vibration of the pyrrolidine ring present in the PVP (poly-N-vinylpyrrolidone) moiety. As no additional peak was observed at 3400 cm⁻¹ and because the FTIR amide peak was observed within the 1650 - 1750 cm⁻¹ range, the presence of a tertiary amide was concluded. In addition, for both sorbents, peaks at 1600 and 1510 cm⁻¹ confirmed the occurrence of aromatic hydrocarbons [C=C] belonging to the divinylbenzene co-polymer.

Complementary to the FTIR spectra, the Raman spectra also provided qualitative and quantitative information on the functional groups of the two sorbents (Figure 1). Raman analysis revealed and confirmed the presence of carboxyl [-COOH] moieties in the hydrophilic DVB co-polymer, i.e. a peak at 1409 cm⁻¹ was observed [34]. In addition, the occurrence of the Oasis HLB® vinyl-groups [CH₂=CH₂] was confirmed as we observed a Raman peak at 1229 cm⁻¹. Aside from the Raman peaks at 1409 cm⁻¹ and 1229 cm⁻¹, in general, similar spectra were observed for both the hydrophilic DVB and Oasis® HLB co-polymers. However, more intense signals were marked for the hydrophilic DVB functional groups, revealing a higher degree of cross-linkage and functionalisation for hydrophilic DVB as compared to Oasis® HLB, offering an explanation for the higher extraction efficiencies for steroidal EDCs, pharmaceuticals, pesticides and personal care products that have generally been observed for hydrophilic DVB versus Oasis® HLB [16,27].
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 phases 35. Average mass balances (%) and corresponding analytical repeatabilities (% RSD) of the different time points in equilibrium (constant Ksw) 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 Ksw 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 Ksw. All organic contaminants studied in this work reached sorption equilibrium between 12 and 24h. The calculated log transformed Ksw 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
terbutylazine (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. Oasis™ 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 Oasis™ 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. 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 Oasis$^{TM}$ HLB.

In line with the ever-increasing number of chemicals that is released into the environment $^{1}$, 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-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 phthalates $^{41}$. 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 ($R_{adj}^2=0.33$, $n=115$, 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 17α- while 5.39 was determined for 17β-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)\(^\text{16}\).

**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°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: 11β-hydroxyandrosterone (j), estrone (k), norgestrel (l), 17α-testosterone (m), 17α-
acetoxyprogesterone (n) and β-zeranol (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 $\Delta H$ 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 chemisorption $^{48}$. The largest negative enthalpies were observed for the steroidal
EDCs ($\Delta H = -113$ kJ mol$^{-1}$), followed by $\Delta H_{phthalates} = -92$ kJ mol$^{-1}$, $\Delta H_{alkylphenols} = -56$ kJ mol$^{-1}$,$\Delta H_{personal \ care \ products} = -32$ kJ mol$^{-1}$, $\Delta H_{pesticides} = -25$ kJ mol$^{-1}$ and $\Delta H_{pharmaceuticals} = -13$
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 testing\(^{50}\).

Figure 4. Thermodynamic parameters, i.e. change in enthalpy (\(\Delta H\)), change in entropy (\(\Delta S\)) and change in free Gibbs energy (\(\Delta G\)) during sorption for the alkylphenols, personal care products, pesticides, pharmaceuticals, phthalates and steroidal EDCs.

The steroidal EDCs also demonstrated a negative \(\Delta S\) (\(\Delta S_{\text{steroidal EDCs}} = -23\) J mol\(^{-1}\) 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 \( \Delta H \) and mainly positive \( \Delta S \) values were observed. Vinmonses et al. (2009) suggested that positive \( \Delta S \) values mark structural changes taking place on the sorbent, and as such increase randomized binding during sorption \(^{53}\). 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 Vinmonses 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 sorbent \(^{53-55}\), 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-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 pharmaceuticals \(^{56}\). Only for strong cationic (rimantadine and trimethoprim) and strong anionic compounds (i.e. sulfadoxine, sulfamethazine, sulfamethoxazole and clorfluric 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 tendancy 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 $\Delta H$ (kJ/mol), entropy $\Delta S$ (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 in lack-of data points for constructing a reliable Box-Behnken design.

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DVB, Hydrophilic divinylbenzene; SPE, solid-phase extraction; Ksw, 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.

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Retaining ring
Screen
Glass fibre filter
Hydrophilic DVB
Glass fibre filter
Screen

FTIR Transmittance (%)
Wavenumber (cm⁻¹)

Raman Intensity (a.u.)

Characterization

Equilibrium sorption

Log K_{sw}

steroidal EDCs
phthalates
pesticides
pharmaceuticals
personal care products
(alkyl)phenols
polyphenol