

# Quantifying the Effects of Temperature and Salinity on Partitioning of Hydrophobic Organic Chemicals to Silicone Rubber Passive Samplers

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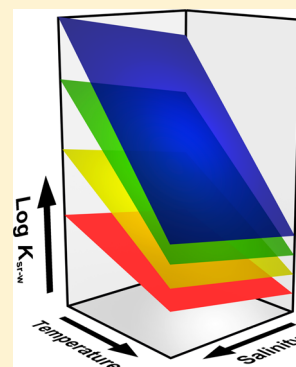
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## Supporting Information

**ABSTRACT:** Nowadays, passive sampling is a widely applied technique to determine freely dissolved aqueous concentrations of hydrophobic organic chemicals (HOCs), such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). Crucial to the measurements are sampler-water partition coefficients, which are generally determined in the laboratory under “standard conditions” (in freshwater at 20 °C). Theoretically, however, the coefficients are dependent on environmental conditions, such as temperature and salinity. Yet, there are insufficient experimental data in the scientific literature to prove this for different polymers. Several polymers are already being applied during field monitoring, however, and neglecting any effects may lead to imprecise results. In the present study, we therefore quantified the effects of temperature and salinity on the sampler-water partition coefficients of PAHs and PCBs for silicone rubber, a material used in Dutch passive sampling monitoring campaigns. The results demonstrated a chemical-specific and hydrophobicity-dependent temperature effect, being independent of salinity, and a chemical- and temperature-independent salinity effect. Based on the obtained data, location-specific silicone rubber–water partition coefficients ( $K_{sr-w}$ ; adjusted for temperature and salinity) can be calculated. The impact of applying such location-specific values was demonstrated using the Dutch passive sampling field monitoring database, covering ten years of PAH and PCB data for several locations. Adjusting the  $K_{sr-w}$  values resulted in aqueous concentrations that were lowered by a factor of 1.6 on average. The reduction was rather constant because of the manner of sampling (under nonequilibrium conditions and using performance reference compounds) and calculating. When sampling under equilibrium conditions in seawater at temperatures at about freezing, and/or applying different calculation approaches, the adjustment effect can potentially increase up to a factor of about 5–6 for the more hydrophobic PAHs and PCBs. Although this study exclusively focused on silicone rubber, qualitatively the results will also apply to other passive sampling materials.



## INTRODUCTION

Passive sampling is considered a valuable and mature technique for determining freely dissolved concentrations of hydrophobic organic chemicals (HOCs) in sediment and soil pore water,<sup>1</sup> as well as in surface water.<sup>2</sup> Different polymer sampling materials can be used for this purpose, including polydimethylsiloxane (PDMS), low-density polyethylene (PE), and polyoxymethylene (POM).<sup>1</sup> In most cases, successful application of passive sampling relies, among other things, on the quality of the parameters quantifying the partitioning behavior of the target chemicals between the sampler material and water, i.e., the polymer–water partition coefficient,  $K_{p-w}$ . Therefore, considerable effort is put into measuring and modeling this parameter for a variety of chemicals and the different sampling polymers.<sup>3–7</sup> Generally, measuring and modeling  $K_{p-w}$  values is performed at ambient or standard conditions, even though from theory it is known that environmental conditions can influence partitioning of chemicals between water and a liquid

or solid phase. For instance, the partitioning of polar and ionizable chemicals between water and a polymer may be dependent on the environmental pH and the concentration of competing sorbates or ions.<sup>8</sup> Similarly, even the partitioning of nonpolar, nonionic HOCs, such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs), is dependent on environmental conditions, predominantly temperature and salinity.<sup>9</sup> According to theory (thermodynamic laws),<sup>9</sup> partitioning of HOCs from water to a solid (or organic solvent) phase increases with a decrease in temperature and an increase in salinity. In both cases, the aqueous solubility of HOCs is reduced, as a result of which their hydrophobicity and thereby their affinity for a hydrophobic phase, such as a

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polymer, increases. For this reason, researchers have suggested and performed adjustments of  $K_{p-w}$  values to site- or experiment-specific conditions, based on calculations using the Van 't Hoff equation to correct for the effect of temperature<sup>3,10</sup> and the empirical Setschenow relationship to correct for the effect of salinity.<sup>10,11</sup> Others have attempted to experimentally quantify the actual effects for a specific polymer.<sup>2,10,12–17</sup> Although one would expect the effects to be similar for different polymers, as they presumably are mostly driven by an alteration of the aqueous solubility and not by a change in polymer characteristics,<sup>3,16</sup> contrasting information has been obtained by different researchers for different polymers. For instance, the absence of a significant temperature effect has been reported for PAH partitioning to PDMS and POM,<sup>12</sup> PAH partitioning to PE,<sup>10</sup> and sorption of triclosan and some nonyl- and octylphenols to PE.<sup>14</sup> In contrast, substantial effects in agreement with theory have been observed for partitioning of low-molecular-weight PAHs and PCBs to PE<sup>2,13</sup> and PAH partitioning to PDMS,<sup>15</sup> whereas effects contrary to theoretical expectations (i.e., reversed effects) have been described for sorption of methyl-triclosan, *n*-nonylphenol, and some high-molecular-weight PAHs and PCBs to PE.<sup>13,14</sup> Similarly, no (significant) effect of salinity on PE-water partitioning of methyl-triclosan, *n*-nonylphenol, PAHs, and PCBs has been reported,<sup>10,14,17</sup> while a significant effect was found for the partitioning of PAHs to PE and PDMS.<sup>2,16</sup> In summary, there is no scientific consensus on the existence, extent, and generality of the effects of temperature and salinity on the partitioning of HOCs between water and different polymers. Moreover, it is yet unclear whether any effects are equal for different chemicals<sup>16</sup> or are dependent on e.g. molecular size.<sup>9,18</sup>

Recently, Reitsma et al.<sup>10</sup> specifically highlighted the experimental challenges in determining  $K_{p-w}$  values for HOCs as a function of temperature and salinity. The potential to deal with these challenges may possibly be the underlying cause of the contrasting findings, although it cannot be excluded that different polymers respond differently to a change in environmental conditions.

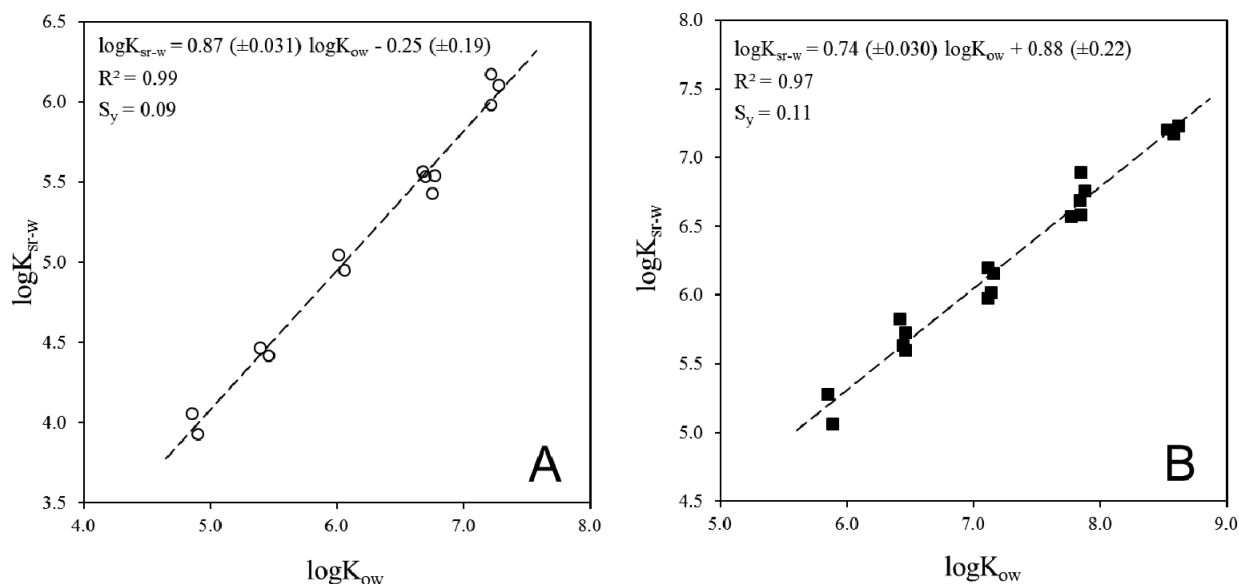
In The Netherlands, freely dissolved HOC concentrations in several coastal and inland surface waters have been monitored since 2002 by using passive samplers consisting of silicone rubber,<sup>19</sup> a material closely resembling PDMS in terms of chemical and partitioning properties.<sup>20</sup> The derivation of the concentrations from the mass accumulated in the samplers during field deployment is based on silicone rubber–water partition coefficients ( $K_{sr-w}$ ) determined under standard conditions (20 °C; no salt), as reported by Smedes et al.<sup>4</sup> Because the sampling locations include both estuarine and fresh water systems and sampling is performed during different seasons (i.e., at different temperatures), it may be important to consider the effects of environmental conditions on  $K_{sr-w}$ . The present study was undertaken in an attempt to quantify the effects of temperature and salinity on the  $K_{sr-w}$  of a series of HOCs being monitored routinely, i.e., PAHs, PCBs, hexachlorobenzene (HCB), and hexachlorobutadiene (HCBd). In the literature, any effects of both factors are generally implicitly considered independent. However, in the present study, the variables were studied both singularly and in combination, in order to investigate any combined or interacting effects. Finally, using actual passive sampling field monitoring data, the influence of adjusting  $K_{sr-w}$  for temperature and salinity on the derived freely dissolved concentrations was investigated.

## MATERIALS AND METHODS

**Chemicals and Sorbents.** Solvents used were acetone and *n*-hexane (Pesti-S grade; Biosolve, The Netherlands), methanol (HPLC supra gradient grade; Biosolve), ethyl acetate (Pestiscan; Lab Scan, Ireland), and acetonitrile (HPLC-S grade; Biosolve). Salts used were sodium chloride (NaCl), sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>), sodium tetraborate (Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>), calcium chloride (CaCl<sub>2</sub>·2H<sub>2</sub>O), strontium chloride (SrCl<sub>2</sub>·6H<sub>2</sub>O), sodium carbonate (NaHCO<sub>3</sub>), potassium chloride (KCl), potassium bromide (KBr), magnesium chloride (MgCl<sub>2</sub>·6H<sub>2</sub>O), and sodium azide (NaN<sub>3</sub>). All salts were of extra pure quality and were obtained from Merck (Darmstadt, Germany), Riedel-de Haën (Seelze, Germany), Aldrich, or Fluka (Steinheim, Germany). Target compounds (PAHs, PCBs, HCB, HCBd; all >98%) were purchased from AccuStandard (New Haven, CT, USA), LGC Standards (Wesel, Germany), or Sigma-Aldrich (Seelze, Germany). A silicone rubber sheet was obtained from Altecweb (AlteSil translucent; thickness 500 μm). It was cleaned from background contamination and oligomers by Soxhlet-extraction with ethyl acetate (100 h) and *n*-hexane (5 h), respectively. After air-drying, 2, 2.5, and 3 mg pieces were cut from the sheet with a razor blade and stored in a glass vial for a week. Prior to the start of the partitioning experiments, the pieces were washed three times with methanol by shaking at 180 rpm for 30 min, after which they were air-dried for 2 h.

**Partition Experiments.** Silicone rubber–water partitioning was determined at 4 different temperatures (4, 12, 20, and 30 °C) and 3 different salinity levels (0, 18, and 36 g/L [%]), representing freshwater, “brackish” water, and seawater, respectively). Dishwasher-washed 250 mL amber-colored glass bottles were washed twice with ultrapure acetone and twice with Millipore water, respectively. Then, a piece of silicone rubber with a predetermined weight was added to each bottle, followed by the addition of an aqueous solution, leaving sufficient headspace for agitation. The aqueous solution consisted of Millipore water containing 50 mg/L of sodium azide (biocide) and various salts in the case of the 18 and 36 % systems. The exact composition was adopted from Jonker and Muijs<sup>16</sup> and is provided in Table S1. The bottles were spiked with 50 μL of a cocktail solution of the test compounds in acetone (concentrations listed in Table S2), after which they were swiftly closed with glass stoppers and immediately placed on a reciprocal shaker table operating at 150 rpm. After 2 weeks of shaking at 20 °C in the dark (to allow an initial distribution at a temperature at which the likelihood of precipitation was smaller than at lower temperatures), bottles were either left at these conditions for another 10 weeks, or placed on a shaker table, operating at 150 rpm in the dark in temperature-controlled rooms of 4, 12, or 30 °C for 10–11 weeks. The overall shaking time of 12–13 weeks was considered sufficient for attaining equilibrium between silicone rubber and water, as this period is longer than that applied by others who have demonstrated or advocated equilibrium conditions.<sup>2,4,6,15–17</sup> Each treatment (combination of temperature and salinity level) was replicated four times. Each shaker table also received three systems containing either 0, 18, or 36 % water, in which the temperature and the temperature- and salinity-specific density were measured upon finishing the equilibrations.

**Extractions.** At the end of the equilibration period, both the aqueous phase and the silicone rubber sampler from each bottle were extracted. Bottles were kept at the equilibration



**Figure 1.** Logarithmic silicone rubber–water partition coefficients ( $\log K_{sr-w}$ ) determined under standard conditions (20 °C; no salt) against octanol–water partition coefficients ( $\log K_{ow}$ ; 20 °C) for PAHs (panel A) and PCBs (panel B). Error bars are omitted for clarity, as they were hardly visible and therefore only obscured the markers.  $S_y$  is the standard error of the predicted  $y$  values for each  $x$  in the regression.

temperature until just prior to opening. About 230 mL of the aqueous phase was transferred to an aluminum foil-covered volumetric cylinder with a glass stopper, containing 15 mL of *n*-hexane, and weighed. The silicone rubber sampler was then removed from the bottle with tweezers, quickly rinsed with Millipore water, dried with a tissue, and transferred to an amber-colored autosampler vial filled with 0.8 mL of acetonitrile. The aqueous phase was extracted by intensively manually shaking the volumetric cylinders for 5 min, after which the hexane phase was transferred to a 100 mL amber-colored pointed flask, using a glass pipet. The extraction of the aqueous phase was then repeated twice with 12 mL of *n*-hexane, and the extracts were collected using the same glass pipet. The extracts from each system were pooled and reduced in volume to 0.5 mL by using a modified Kuderna-Danish apparatus and nitrogen gas, respectively. The extracts were then solvent-exchanged to 0.4 mL of acetonitrile. Depending on the volume, all extracts finally received 0.5 or 1  $\mu\text{g}$  of 2-methylchrysene and 0.05 or 0.1  $\mu\text{g}$  of PCB-209 (internal standard solutions in acetonitrile). The aqueous phase extractions were accompanied by four blank and four recovery determinations. Blanks concerned the processing of 39 mL (i.e., 15 + 12 + 12 mL) of *n*-hexane in a pointed flask as described above, and for the recovery determinations, 230 mL of Millipore water was spiked with a cocktail solution of the test compounds in acetone, extracted, and processed as described above. In addition, 4 pieces of original, cleaned silicone rubber served as blanks for the silicone rubber extractions. All vials with silicone rubber samplers were vortexed for 2 min, and all extracts were finally stored at –20 °C. Prior to the analyses, vials were kept at room temperature for a day and vortexed for another 30 s.

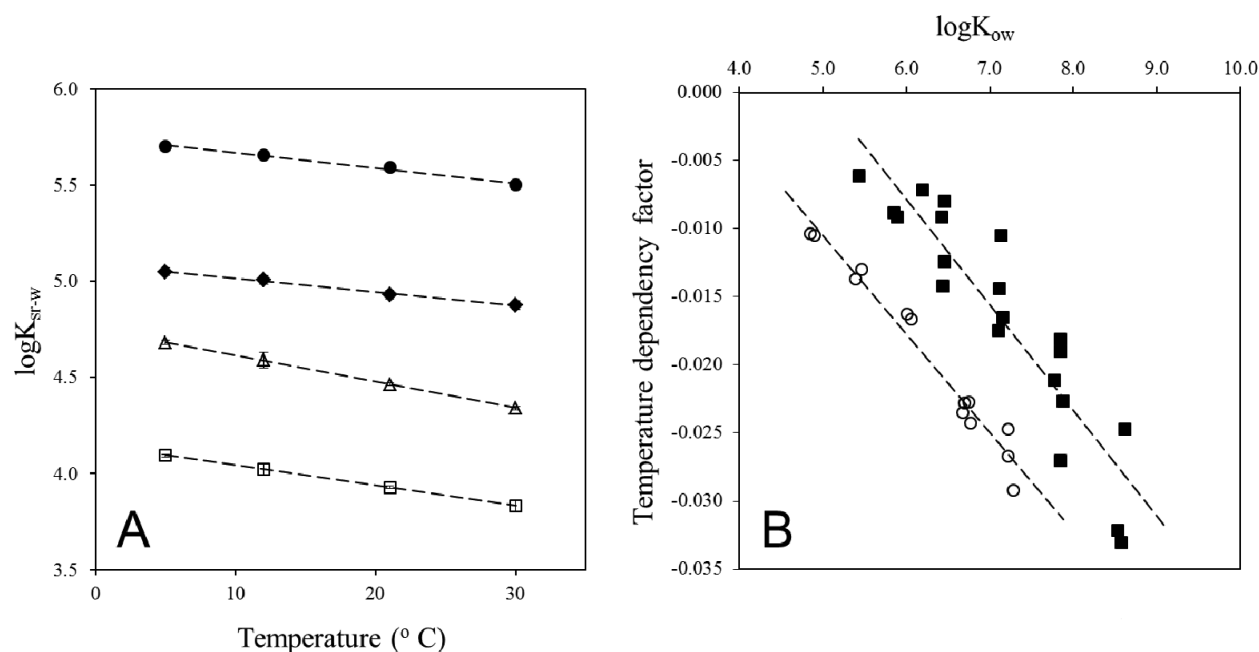
**Chemical Analysis.** PAH concentrations in all extracts were analyzed by HPLC as described previously.<sup>16</sup> PCBs, HCB, and HCBd were analyzed by injection of 1  $\mu\text{L}$  in the split mode on a Thermo Scientific Trace GC Ultra, equipped with a Triplus autosampler, an ECD detector, a polar precolumn, and a Zebtron ZB-SMSi analytical column (Phenomenex; 30 m  $\times$  0.25 mm; 0.25  $\mu\text{m}$  film thickness). Quantification in both cases

was performed using 5 calibration standards (levels) in acetonitrile.

**Data Analysis.** Internal standard-corrected concentrations in silicone rubber extracts were converted to concentrations in silicone rubber ( $C_{sr}$ ), using the sampler masses (silicone rubber blanks did not contain any detectable target compounds). Likewise, internal standard-, blank-, and recovery-corrected concentrations in the aqueous phase extracts were converted to aqueous concentrations ( $C_w$ ), using the masses and temperature- and salinity-specific densities of the aqueous phases. Silicone rubber–water partition coefficients ( $K_{sr-w}$ ) were then calculated by dividing  $C_{sr}$  by  $C_w$ . Differences between treatments were tested for significance by using *t*- or *F*-tests ( $\alpha = 0.05$ ) in Prism GraphPad 6.04. Octanol–water partition coefficients ( $K_{ow}$ ; 20 °C) used for comparison were calculated by SPARC (version October 2011, release w4.6.1691-s4.6.1687; retrieval date values: November 27, 2013).

## RESULTS AND DISCUSSION

**$K_{sr-w}$  Values Determined under Standard Conditions.**  $\log K_{sr-w}$  values determined in this study at different temperatures and salinities are listed in Table S3 of the Supporting Information. In Figure 1, the values measured under standard conditions (20 °C, no salt) are plotted against  $\log K_{ow}$  values. For both PAHs and PCBs, a linear and highly significant correlation between the two parameters exists, having an  $r^2$  of 0.99 (PAHs) and 0.97 (PCBs). These highly significant correlations once more confirm that partitioning of PAHs and PCBs to silicone rubber is a process predominantly driven by hydrophobicity<sup>21</sup> and suggest that the experiments were performed adequately. Other observations that support the reliability of the data determined under standard conditions include mass balances close to 100% (97  $\pm$  4% for PAHs and 103  $\pm$  3% for PCBs) and the generally very low standard deviations of the  $\log K_{sr-w}$  values (see Table S4). The linear character of the regression curves in Figure 1 also suggests that the standard condition systems were at equilibrium after the 12-week equilibration time (as expected; see the Material and



**Figure 2.**  $\log K_{sr-w}$  for selected compounds determined in the absence of salt as a function of temperature (panel A:  $\square$  phenanthrene,  $\Delta$  pyrene,  $\blacklozenge$  HCB,  $\bullet$  PCB-52); and the temperature dependency factor of PAHs (open markers) and PCBs, HCB, and HCBd (closed markers) as a function of the compounds'  $\log K_{ow}$  (panel B). The dashed lines in graph B are regression lines with equations: *temperature dependency factor* =  $-0.0072 \log K_{ow} + 0.026$  (PAHs;  $r^2 = 0.97$ ) and *temperature dependency factor* =  $-0.0078 \log K_{ow} + 0.039$  (PCBs;  $r^2 = 0.84$ ).

Methods section). After all, in the case of nonequilibrium, the curves would have shown a leveling off for the more hydrophobic compounds. For the other (nonstandard condition) systems, several regression curves (i.e., those for lower temperatures and higher salinities) do show such a leveling off or a downward curvature; this will be discussed below.

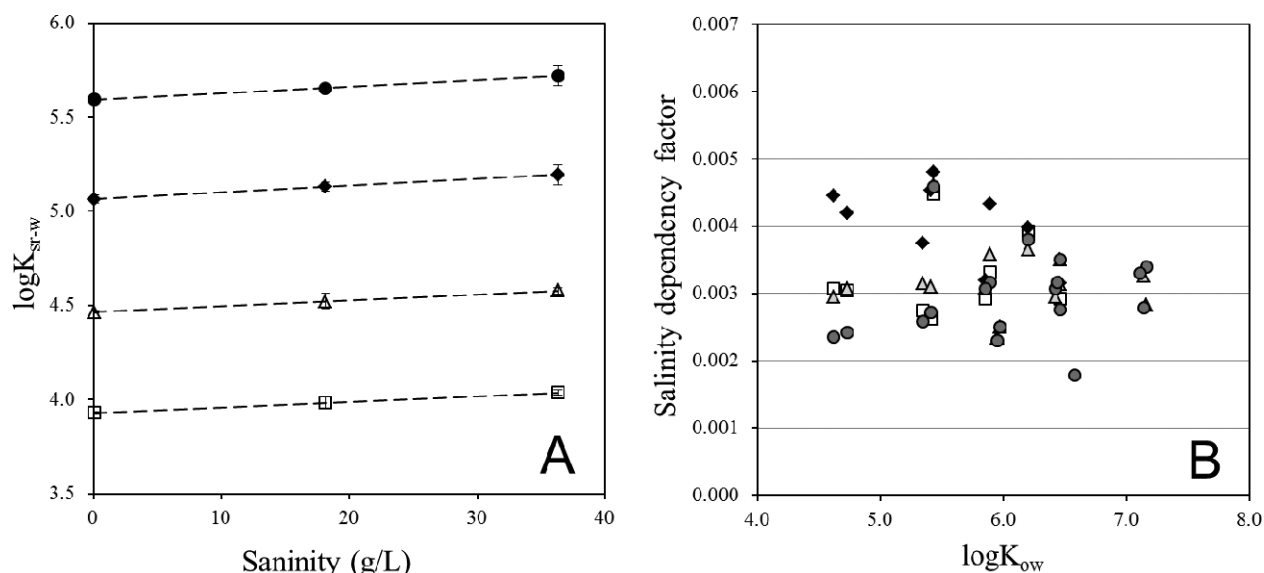
Silicone rubber is a material that has been used in environmental monitoring and experiments.<sup>19,21–26</sup>  $K_{sr-w}$  values are however available from only a limited number of literature sources,<sup>4,21,25,27</sup> which all relate to standard conditions (20  $^{\circ}C$ , no salt). Figure S1 presents a comparison with literature data available for AlteSil silicone rubber,<sup>4,21,25</sup> i.e., the material also used in the present study and the Dutch passive sampling monitoring program. The current data compare rather well with those from Ter Laak et al.<sup>25</sup> (average absolute difference of 0.17 log units;  $n = 10$ ); data also determined with a batch-shake setup. Similar differences are observed when comparing with the data from Smedes et al.<sup>4</sup> (average absolute difference 0.18 log units;  $n = 26$ ), but much larger differences exist with the data from Yates et al.<sup>21</sup> (average absolute difference 0.48 log units;  $n = 23$ ). Both the latter data sets were obtained with the cosolvent method. The differences between the current data set and the data from Smedes et al. are discussed in more detail in the Supporting Information, as the latter data set is often used as a standard/reference set<sup>22,23</sup> and is also applied to the passive sampling monitoring in The Netherlands.

**Effect of Temperature on  $K_{sr-w}$ .** The effect of temperature on silicone rubber–water partitioning was determined at three different salinity levels. For the less hydrophobic chemicals (i.e., HCB, HCBd, the 3- and 4-ring PAHs, and PCBs 18, 28, and 52), the change in  $\log K_{sr-w}$  per  $^{\circ}C$  as quantified by the slope of the  $\log K_{sr-w}$  – temperature plots, was similar at the three salinity levels (see Table S5). Although differences can be observed between the three salinity treatments, these are relatively small (only for phenanthrene, anthracene, and

chrysene, the values determined at 36 ‰ salinity differed significantly (*F*-test) from the values determined at lower salinities), and no obvious trends exist. For the remainder of the chemicals, i.e., the more hydrophobic ones, the  $K_{sr-w}$  values at the lower temperatures and high salinity levels were considered not reliable, as will be discussed below, and the effect of temperature could not be quantified in these cases.

Based on the data for the less hydrophobic compounds, we hypothesize that the effect of temperature on silicone rubber–water partitioning of PAHs and PCBs is independent of the salinity of the aqueous phase. Hence, the following discussion is based on the effect of temperature as determined in 0 ‰ water (i.e., only  $\text{NaN}_3$  present). For this salinity level, the temperature effect could be quantified for all test compounds, although this still required omitting the data obtained at 4  $^{\circ}C$  for the 6-ring PAHs and the more hydrophobic PCBs, as well as the 12  $^{\circ}C$  data for the three most hydrophobic heptachlorinated biphenyls. These data were considered biased and unreliable as they showed leveling/cutoff behavior (see Figure S3), indicating experimental artifacts, such as nonequilibrium conditions, solubility issues, or third phase effects (discussed in more detail in the next section).

The relationship between temperature and  $K_{sr-w}$  is illustrated in Figure 2A for various (less hydrophobic) compounds. This figure shows that the observed effect is according to theoretical expectations: with a decrease in temperature, partitioning to silicone rubber increased. As outlined in the Introduction, a similar effect has previously also been found for PAH partitioning to PDMS<sup>15</sup> and partitioning of low-molecular-weight compounds to PE.<sup>2,13</sup> The figure also demonstrates that the temperature effect is chemical-dependent, as the slopes of the four relationships in Figure 2A differ. When plotting the slopes of the relationships, hereafter referred to as the temperature dependency factor for  $K_{sr-w}$ , of all chemicals against the chemicals'  $\log K_{ow}$ , a linear relationship is observed



**Figure 3.**  $\log K_{sr-w}$  for selected compounds determined at 20 °C as a function of salinity (panel A:  $\square$  phenanthrene,  $\Delta$  pyrene,  $\blacklozenge$  PCB-18,  $\bullet$  PCB-52); and the salinity dependency factor of PAHs, PCBs, HCB, and HCBd at different temperatures (4 °C black diamonds; 12 °C open squares; 20 °C light gray triangles; 30 °C dark gray circles) as a function of the compounds'  $\log K_{ow}$  (panel B).

(see Figure 2B). This figure clearly indicates that the temperature dependency factor becomes more negative with hydrophobicity, as previously observed for PAH sorption to PDMS.<sup>15</sup> The temperature dependency factor varies between about  $-0.01$  and  $-0.03$  log units per °C for PAHs and  $-0.005$  and  $-0.035$  log units per °C for PCBs. For PAHs, the factors, as well as the accompanying thermodynamic parameters (i.e., changes in Gibbs free energy ( $\Delta G$ ), enthalpy ( $\Delta H$ ), and entropy ( $T\Delta S$ ), as calculated according to eqs 2–4 in ref 15), are very close to the ones derived in ref 15 (see Table S6). This indicates that sorption of these chemicals to silicone rubber and PDMS is very similar in terms of thermodynamics.

Two interesting observations can be made from Figure 2B. First of all, although the slopes of the relationships for PAHs and PCBs are similar, the intercepts are not (see equations in the figure caption). This implies that at any given hydrophobicity, partitioning of PAHs to silicone rubber is influenced by temperature changes to a larger extent than that of PCBs. The exact cause of this phenomenon is unclear. Second, based on the (extrapolation of the) linear regression curves in Figure 2B, for PCBs and PAHs with a  $\log K_{ow}$  of about 5 and 3.5, respectively, no effect of temperature (i.e., a dependency factor of 0) is expected, whereas for compounds with even lower hydrophobicity, a positive effect would be anticipated. Alternatively, the relationships in Figure 2B may level off at lower hydrophobicities (stabilizing at a dependency factor close to or at 0). Additional experiments would be required to test this.

**Effect of Salinity on  $K_{sr-w}$ .** The current experimental setup allowed the evaluation of the effects of salinity on  $K_{sr-w}$  at four different temperatures. Generally, for the less hydrophobic compounds the effect did not differ significantly (*F*-test) at the different temperatures (HCBd, HCB, fluoranthene, PCBs 18, 28, and 52 at all temperatures; phenanthrene, anthracene, and pyrene at the three highest temperatures; and benz[*a*]anthracenes, chrysene, PCBs 66, 72, 101, and 103 at the highest two temperatures). For phenanthrene, anthracene, and pyrene, the effect at 4 °C was however significantly (*F*-test) higher than at the three higher temperatures. Although the effect is

somewhat variable for the less hydrophobic compounds, a clear trend with hydrophobicity is not observed (see Table S7). In Figure 3A, the effect determined at 20 °C is illustrated for four of these chemicals. Again, the effect is according to expectations: partitioning to silicone rubber is enhanced at higher salinity levels. For the remaining, more hydrophobic compounds, however,  $K_{sr-w}$  values decreased with increasing salinity (see Figure S3). In most cases this occurred only at the highest salinity level tested, but for most hydrophobic chemicals, already at 18‰ the  $K_{sr-w}$  was lower than measured for the 0‰ systems. Although a similar phenomenon has been observed before,<sup>10</sup> it is incompatible with theory and thus most probably based on an experimental artifact. Note that this statement is supported by the fact that the standard deviations of the data concerned are often elevated (Table S3). The presumed artifact may be caused by one or a combination of the following factors: (i) the increased presence of organic matter, introduced through the addition of the salts that contain this material as contamination. Any dissolved organic material would cause increased aqueous concentrations and thus lowered  $K_{sr-w}$  values. Organic matter analyses however resulted in levels below quantification limits for all three salinity systems; hence, this explanation remains hypothetical; (ii) nonequilibrium conditions for the more hydrophobic chemicals. Reitsma et al.<sup>10</sup> recently suggested that equilibrium times may increase with a reduction in temperature and an increase in salinity through the increase in water viscosity of the aqueous boundary layer surrounding the passive sampler material. For the currently applied temperature and salinity range, the change in the aqueous viscosity is such<sup>28</sup> that a reduction in the aqueous diffusion coefficient of a factor of about 2 can be estimated.<sup>29</sup> Also note that the diffusion within silicone rubber is expected to be reduced by a factor of about 3 when lowering the temperature from 20 to 4 °C.<sup>30</sup> The diffusion in this polymer is however so fast (equilibration within hours<sup>31</sup>) that a factor of 3 reduction cannot contribute to any nonequilibrium conditions. As such, diffusion through the aqueous boundary layer is rate-limiting and dominates the overall equilibration process. The reduced aqueous diffusion may therefore

contribute to explaining the deviation from linearity observed for the most hydrophobic compounds at the lowest temperature. Still, it is by far not sufficient to explain the leveling off/cutoff behavior of over an order of magnitude at the higher salinity levels (also at the higher temperatures; see Figure S3). Hence, the leveling/cutoff behavior is most probably caused by (iii) solubility problems. The aqueous solubility of HOCs decreases with salinity. Compounds for which  $K_{sr-w}$  values appear biased may have precipitated upon spiking. The slow dissolution kinetics of the solid phase compounds may have resulted in residual precipitates at the time of sampling. This material would be extracted along with the freely dissolved chemicals during the water phase extractions, which would cause an overestimation of  $C_w$  and thus an underestimated  $K_{sr-w}$ .

Solubility problems are plausible because the deviation from linearity of the relationship between  $\log K_{sr-w}$  and salinity was most pronounced at the lowest temperature (at 30 °C, the deviation occurred only at higher hydrophobicities; see Figure S3) and for compounds with the lowest aqueous solubility, i.e., dibenz[*a,h*]anthracene and the coplanar PCBs (PCB-126 and -169), for which also “the first” deviations can be observed. In case the artifact would be caused by organic matter or nonequilibrium conditions, these compounds should have displayed behavior similar to that of compounds with similar hydrophobicity, unless any organic matter concerned graphitized material, to which coplanar PCBs sorb exceptionally strong.<sup>32</sup> The presence of such material could however not be detected (see above), is unlikely, and does not explain the deviating behavior of dibenz[*a,h*]anthracene.

In any case, the present results do once more stress the challenges in determining polymer–water partition coefficients of very hydrophobic chemicals at low temperatures and/or high salinities.<sup>10</sup> A way to deal with these challenges may be to apply dosing via loaded samplers in order to avoid precipitation. To verify equilibrium conditions, different sampler thicknesses and/or sampling at different time points could be applied.

Based on the present data for the less hydrophobic compounds and the previous data for PDMS<sup>16</sup> that showed a similar salinity effect for all PAHs, we infer that the effect of salinity on the  $K_{sr-w}$  is independent of temperature and hydrophobicity. Temperature-independent behavior is consistent with previous results showing no significant variation with temperature in the effect of salinity on the aqueous solubility of anthracene.<sup>33</sup> In Figure 3B, the conclusion is illustrated by plotting the increase in  $\log K_{sr-w}$  per unit of salinity (g/L), hereafter referred to as the salinity dependency factor, as determined at different temperatures for unbiased systems (i.e., those systems showing a salinity effect according to expectations: an increase in  $K_{sr-w}$  with increasing salinity; see Table S7), as a function of the  $K_{ow}$ . The data in the figure do not reveal any clear trend and, despite the appreciable scatter, suggest a constant value for the dependency factor. The averaged value for the salinity dependency factor derived on the basis of the unbiased data measures  $0.0033 \pm 0.00066$  log units per unit of salinity (g/L). Remarkably, this factor is significantly (*t*-test) smaller than the one derived for PDMS-coated SPME fibers, which measured  $0.0053 \pm 0.00042$  based on the data for all PAHs.<sup>16</sup> The same applies to the Setschenow (salting out) constants calculated on the basis of both data sets: whereas the previously derived averaged value measured 0.35 L/mol,<sup>16</sup> the currently derived averaged value is 0.19 L/mol. The cause of this discrepancy is not clear, since both studies were performed

in one lab, using the same salts and a similar experimental setup. Although one would not expect salts to have any effect on (the sorption properties of) a polymer, but only on the aqueous solubility,<sup>16</sup> this result may suggest otherwise. We stress this hypothesis is speculative, and dedicated experiments would be required to support or invalidate it.

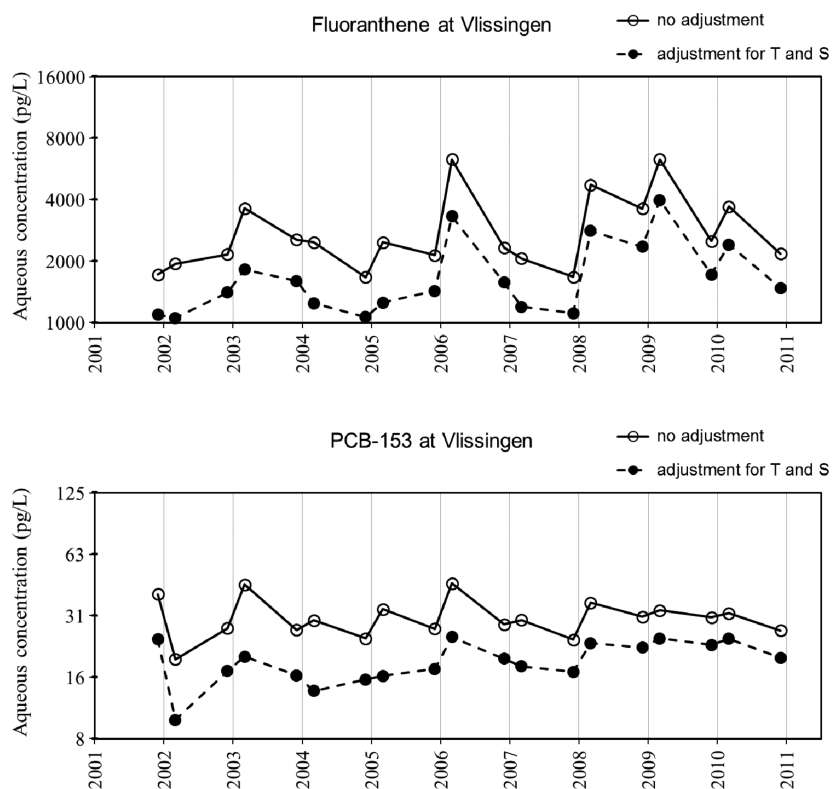
**Joint Effect of Temperature and Salinity on  $K_{sr-w}$ .** The above-discussed results demonstrate there is a significant effect of both temperature and salinity on silicone rubber–water partitioning of HOCs. The effects of both parameters appear to be independent and noninteracting, as salinity effects are similar at different temperatures and temperature effects are similar at different salinity levels. Since (i) the salinity effect is independent of chemical properties and (ii) the temperature effect does depend on chemical properties, it is possible to calculate condition-specific silicone rubber–water partition coefficients ( $K_{sr-w}(T,S)$ ) by correcting  $K_{sr-w}$  values determined under standard conditions (20 °C, no salt;  $K_{sr-w}(20,0)$ ) according to

$$\log K_{sr-w}(T, S) = \log K_{sr-w}(20, 0) + \gamma \cdot (T - 20) + 0.0033 \cdot S \quad (1)$$

with  $T$  being the temperature in °C,  $S$  being the salinity in g/L, and  $\gamma$  being the (negative) compound-specific temperature dependency factor. In Table S8, eq 1 is presented for all investigated chemicals. Potentially, the equation could also be used to calculate condition-specific  $K_{sr-w}$  values for other PAHs and PCBs not included in this study. To this end, both  $\log K_{sr-w}(20,0)$  and  $\gamma$  first need to be estimated based on the compounds'  $\log K_{ow}$  values using the relationships presented in Figures 1 and 2B.

The equations in Table S8 show that the overall effect of temperature and salinity is the largest for the most hydrophobic compounds. Differences in  $K_{sr-w}$  determined under standard conditions and those applying to for instance seawater at temperatures near freezing may increase up to a factor of 4.8 (0.7 log units) for indeno[1,2,3-*cd*]pyrene and even 5.8 (0.8 log units) for PCB-180. For the less hydrophobic chemicals investigated, differences are smaller, down to a factor of 1.7 (0.2 log units) for HCBd.

**Implications for Passive Sampling Measurements in the Field.** When applying passive sampling with silicone rubber and determining freely dissolved concentrations, neglecting the effects of temperature and salinity by using  $K_{sr-w}(20,0)$  values will result in imprecise data. In the case of sampling under equilibrium conditions, the difference between actual and reported concentrations will equal  $K_{sr-w}(T,S)/K_{sr-w}(20,0)$  and may thus increase up to the factors mentioned above. This applies to all chemicals and may for instance occur in the lab when performing equilibrium partitioning experiments. However, when sampling in the field, generally only the less hydrophobic chemicals reach equilibrium, while for the more hydrophobic compounds sampling will occur in the linear uptake phase. In such cases, the  $K_{sr-w}$  plays a less dominant role because it is multiplied by the extent to which equilibrium is reached (as derived from the application of performance reference compounds (PRCs) and expressed as a fraction),<sup>2,11,14</sup> or the final freely dissolved concentrations are derived by model calculations in which the so-called “sampling rate” (also estimated from PRC release) dominates.<sup>19,34</sup> Hence, for the more hydrophobic compounds, the “bias” introduced by not correcting for site-specific conditions during field sampling



**Figure 4.** Temporal (2001–2011) concentration profiles (pg/L) of fluoranthene and PCB-153 at the Dutch estuarine location “Vlissingen”, as determined by passive sampling with silicone rubber sheets. Freely dissolved concentrations in the water phase were either calculated with or without adjusting the silicone rubber–water partition coefficients for the effects of location-specific temperature and salinity.

usually will be less than  $K_{sr-w}(T,S)/K_{sr-w}(20,0)$ . To illustrate the impact of (not) adjusting  $K_{sr-w}$  for the effects of temperature and salinity, this section presents a case study based on Dutch field monitoring data. As mentioned in the Introduction, since 2002 several coastal and inland surface waters in The Netherlands are monitored by using passive sampling with silicone rubber. The monitoring database contains freely dissolved concentrations of PAHs and PCBs determined over a period of about ten years and includes concentrations determined in fresh water (in spring to autumn) and seawater (in autumn and winter). The crude data underlying the database were recalculated using the above-derived relationships (see the Supporting Information for details on the calculations).

In Figure 4, results are presented for two compounds sampled at the (estuarine) location “Vlissingen” (fluoranthene and PCB-153; the first (nearly) attained equilibrium during exposure and the uptake of the latter was fully in the linear uptake phase, i.e. far from equilibrium). This figure first of all demonstrates that adjusting  $K_{sr-w}$  for the effects of temperature and salinity lowers the final concentrations. This is a general feature for all locations (see Figure S4 for additional results); the only exception for the Dutch situation would be in the case of fresh water with temperatures  $>20$  °C. Furthermore, as discussed above, the impact of the adjustment is less than the factor  $K_{sr-w}(T,S)/K_{sr-w}(20,0)$ . Actually, the reduction in concentrations is rather limited, ranging from 1.3 to 2.3, with an average of 1.6 (see Figure S6). Also, it appears independent of  $K_{ow}$  for the PAHs and PCBs investigated (see Figure S7A). It should be noted that this behavior is specific to the currently used model calculations (details in the Supporting Information). When using other PRC-based calculation approaches

described in the literature (e.g., ref 11), the reduction in the aqueous concentrations is both more pronounced (up to a factor of  $\sim 3$  for the present monitoring data set) and hydrophobicity-dependent (see Figure S7B). The average factor of 1.6 is similar to the maximum possible reduction for the less hydrophobic compounds (see above), i.e., those that came (close) to equilibrium during the field sampling. Concentrations of the more hydrophobic compounds did not reach equilibrium conditions (by far) during sampling and are thus controlled by the sampling rate, which is inversely related to the  $K_{sr-w}$ . Interestingly, the sampling rate derived from the PRC release increases with temperature, as shown in Figure S5, but adjusting for temperature does not (fully) remove its influence. Since the tidal current is about equal in autumn and winter, the average thickness of the aqueous boundary layer surrounding the silicone rubber is expected to be equal as well, and the increase in sampling rate most probably illustrates the effect of temperature on diffusion through the boundary layer. Finally, applying adjusted  $K_{sr-w}$  data also generally does not remove the seasonal differences in concentrations that are observed at several locations (see Figure S4; concentrations in winter are mostly higher than those in autumn). This suggests that concentrations simply differ for different seasons at these locations.

#### Importance of Correcting for Site-Specific Conditions.

As illustrated above, adjusting passive sampling data for site-specific environmental conditions can have an effect on the final freely dissolved concentrations. Performing the adjustment should therefore be considered when passive sampling is carried out as part of chemical monitoring for trend analysis, to study temporal or spatial variation in freely dissolved concentrations, or for checking compliance with chemical

quality standards. However, when passive sampling is performed in the context of risk assessment and the ultimate goal is to protect organisms, it should be kept in mind that equilibrium partitioning of HOCs to organisms (i.e., the bioaccumulation factor, BAF) also depends on environmental conditions. Just like the  $K_{sr-w}$  described here, BAFs also increase with decreasing temperatures.<sup>15</sup> Therefore, reduced passive sampler-derived aqueous concentrations in for instance winter-time (after adjusting for temperature effects on  $K_{sr-w}$ ) do not necessarily imply reduced risks. After all, in case the temperature-dependence of partitioning to organism lipids is stronger than that of the passive sampling polymer (as is the case for PDMS, and thus probably also for silicone rubber, as these polymers behave similarly in a thermodynamic sense) internal concentrations in biota may actually potentially be higher than in summer.<sup>15</sup>

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Listings of media and spike compositions; silicone rubber–water partition coefficients; derived temperature and salinity dependency factors, thermodynamic parameters, and equations; comparisons with literature data; and field monitoring data. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b00286.

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### Notes

The authors declare no competing financial interest.

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