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Polyethylene–Water and Polydimethylsiloxane–Water Partition Coefficients for Polycyclic Aromatic Hydrocarbons and Polychlorinated Biphenyls: Influence of Polymer Source and Proposed Best Available Values

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Abstract: For most passive sampling applications, the availability of accurate passive sampler–water partition coefficients (K_{p-w}) is of key importance. Unfortunately, a huge variability exists in literature K_{p-w} values, in particular for hydrophobic chemicals such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). This variability is a major source of concern in the passive sampling community, which would benefit from high-quality K_{p-w} data. Hence, in the present study “best available” PAH and PCB K_{p-w} values are proposed for the two most often applied passive sampling materials, that is, low-density polyethylene and polydimethylsiloxane (PDMS), based on (1) a critical assessment of existing literature data, and (2) new K_{p-w} determinations for polyethylene and PDMS, with both polymers coming in six different versions (suppliers, thicknesses). The experimental results indicated that K_{p-w} values for PDMS are independent of the source, thus allowing straightforward standardization. In contrast, K_{p-w} values for polyethylene from different sources differed by up to 30%. Defining best available K_{p-w} values for this polymer therefore may require standardization of the polymer source. Application of the proposed best available K_{p-w} values will substantially improve the accuracy of freely dissolved concentration results by users and the potential for comparisons across laboratories. *Environ Toxicol Chem* 2022;41:1370–1380. © 2022 The Authors. *Environmental Toxicology and Chemistry* published by Wiley Periodicals LLC on behalf of SETAC.

Keywords: Passive sampling; Partition coefficients; Polyethylene; Polydimethylsiloxane; Polycyclic aromatic hydrocarbons; Polychlorinated biphenyls

INTRODUCTION

Passive sampling, that is, partitioning-based, nondepletive extractions with polymers, is an often used technique in environmental analysis for determining freely dissolved concentrations (C_{free}) of organic chemicals in surface water and porewater of sediments and soils. The technique involves the exposure of a specific polymer to an aqueous medium from which dissolved organic chemicals accumulate into the polymeric sampler by means of equilibrium partitioning. This

thermodynamic partitioning process is quantified by conditional and chemical-specific rate constants and polymer–water equilibrium partition coefficients (K_{p-w} ; Ghosh et al., 2014).

Different polymers and sampler formats can be used for sampling, each having different advantages and disadvantages (Jonker et al., 2020) and, to some extent, “chemical domains,” thus having different applications. Most commonly used are polymer sheets made of low-density polyethylene, silicone rubber, and polyoxymethylene (POM); and solid-phase microextraction (SPME) fibers coated with polydimethylsiloxane (PDMS) or polyacrylate (Jonker et al., 2018). For most applications, the availability of reliable K_{p-w} values is critical for obtaining accurate C_{free} values. The experimental determination of K_{p-w} values, however, is challenging (Jonker et al., 2015) and “more difficult than generally assumed” (Booij et al., 2016). This primarily applies to (very) hydrophobic organic chemicals, such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs), ubiquitous chemicals that are

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often targeted in environmental analysis. Most probably because of this reason, polymer-specific K_{p-w} values for PAHs and PCBs available in the literature vary considerably, and the variability increases with chemical hydrophobicity (DiFilippo & Eganhouse, 2010; Lohmann, 2012). This variability is a major source of concern in the passive sampling community (Booij et al., 2016).

When applying passive sampling, researchers either use K_{p-w} values experimentally determined in their own laboratory or experimental values selected from the literature. In addition, quantitative structure–property relationship (QSPR) models can be used to calculate K_{p-w} values (Endo et al., 2011; Ghosh et al., 2014; Lohmann, 2012). However, QSPR-derived K_{p-w} values often largely depend on the values of the independent variable used, which generally is the octanol–water partition coefficient (K_{OW} ; Ghosh et al., 2014; Lohmann, 2012). The K_{OW} values are often associated with (large) uncertainty as well, because their experimental determination is challenging too or they are also modeled. Furthermore, the values used for modeling K_{p-w} may differ from the ones applied to construct the QSPR. All in all, the K_{p-w} selection process by individual researchers inevitably results in a range of values for a specific chemical–polymer combination. In a recent interlaboratory passive sampling comparison study including 11 research laboratories (Jonker et al., 2018), the PAH and PCB K_{p-w} values applied by the participants varied by a factor of up to 7 for PDMS, 13 for polyethylene, and 20 for POM. Despite the availability of “best fit values” for polyethylene published by one of the participants (Lohmann, 2012) and “provisional” values for all three polymers, published by several of the other participants (Ghosh et al., 2014), all participants used values they personally considered the best available ones, that is, values determined themselves or values taken from different literature sources.

The apparent lack of consensus on K_{p-w} values complicates a straightforward and widespread application of passive sampling (Lohmann et al., 2017) and may slow down further implementation of the technique in, for example, monitoring programs on a large scale (Booij et al., 2016). Therefore, the passive sampling community would clearly benefit from a common K_{p-w} data set that could be used by all performers. A complicating factor with such a data set is the fact that different research groups use sampling polymers obtained from different sources, potentially having different compositions, for example, in terms of the nature and degree of polymer cross-linking or levels of oligomers and filling agents (Lohmann, 2012). This may affect the actual K_{p-w} (Perron et al., 2013), perhaps causing part of the observed variability in literature K_{p-w} data, but information on the impact of polymer source on K_{p-w} is scarce. For PDMS and polyethylene, it has been inferred that polymer source “does not significantly impact” K_{p-w} (DiFilippo & Eganhouse, 2010) and “is of minor importance” (Lohmann, 2012). However, these conclusions were drawn based on literature data, and the inherent interlaboratory variation may have obscured actual significant differences between different polymer sources. In single experiments, both Smedes et al. (2009) and Gilbert et al. (2016) demonstrated

that PAH and PCB K_{p-w} values for silicone rubbers from different suppliers can differ by up to several tenths of log units.

The aims of the present study were (1) to investigate whether polymers from different suppliers and having different thicknesses have significantly different K_{p-w} values; to this end, polymer–water partitioning was determined for a series of PAHs and PCBs using six types of polyethylene and six types of PDMS samplers; (2) to review the scientific literature and compile an updated K_{p-w} database for PAHs and PCBs; and (3) to propose, based on the results of the previous two activities, “best available” K_{p-w} values for PAHs and PCBs. The focus was on polyethylene and PDMS, because these polymers are most commonly used, are generally obtained from different suppliers, and have been recommended as standard passive sampling polymers for determining C_{free} in sediments and soils (Jonker et al., 2020).

MATERIALS AND METHODS

Chemicals

The following solvents were used: acetone, dichloromethane, and *n*-hexane (Pesti-S grade; Biosolve), methanol (high-performance liquid chromatography [HPLC] Supra-gradient grade; Biosolve), ethyl acetate (Pestican; Labscan), and acetonitrile (HPLC-S grade; Biosolve). Sodium azide (Merck) was used as a biocide. Target compounds included 13 PAHs and 18 PCBs (purity > 98%), which were purchased from AccuStandard, LGC Standards, or Sigma-Aldrich. PCB-209 (98%; Promochem) and 2-methylchrysene (purity > 99%; Community Bureau of Reference) were used as injection internal standards.

Polymers

New experimental K_{p-w} values were determined for six types of polyethylene and six types of PDMS samplers. The characteristics of these passive sampling materials, including code, supplier, polymer thickness, and core thickness of the SPME fibers, are listed in Table 1. These materials were used previously during the interlaboratory comparison study (Jonker et al., 2018) and include the most frequently applied materials and sources. All polymers and fibers were cut to pieces of desired weight/dimension: 2 mg for sheets and 2–20 cm for fibers. These were cleaned from background contamination and oligomers by shaking with solvents in 20-ml vials on a reciprocal shaker (180 rpm). The polymer-to-solvent ratio was at least 1:1000 in all cases. The polyethylene pieces were successively washed 2 × 30 min with acetonitrile, 2 × 30 min with dichloromethane, and 2 × 30 min with *n*-hexane, after which they were air-dried for 2 h in an ultraclean fume hood/clean laboratory. The PDMS-coated SPME fibers were washed with hexane (1 × 30 min), acetonitrile (2 × 30 min), and Milli-Q water (2 × 30 min), successively. The PDMS sheet (from SSP) was first Soxhlet-extracted for 48 h with ethyl acetate, after which it was air-dried. Then 2-mg pieces were cut from the sheet, and these were washed 2 × 30 min with methanol and air-dried. All

TABLE 1: Characteristics of the passive sampling materials used in the present study

Code	Format	Polymer thickness ^a (μm)	Core thickness (μm)	Supplier
Polyethylene (PE)				
PE-1	Sheet	25		Ace Hardware, Oak Brook, IL, USA
PE-2	Sheet	25		Berry Global, Evansville, IN, USA
PE-3	Sheet	51		Brentwood Plastics, St. Louis, MO, USA
PE-4	Sheet	25		Covalence Plastics, Minneapolis, MN, USA
PE-5	Sheet	25		Berry Global (Film-Gard sheeting), Evansville, IN, USA
PE-6	Sheet	26		VWR International, Leicestershire, UK
Polydimethylsiloxane (PDMS)				
S10-1	SPME fiber	10	200	Polymicro Technologies, Phoenix, AZ, USA
S10-2	SPME fiber	10	200	Fiberguide Industries, Stirling, NJ, USA
S30-1	SPME fiber	30	100	Polymicro Technologies, Phoenix, AZ, USA
S30-2	SPME fiber	30	500	Polymicro Technologies, Phoenix, AZ, USA
S100	SPME fiber	100	200	Fiberguide Industries, Stirling, NJ, USA
SSP	Sheet	100		Shielding Solutions, Great Notley, Essex, UK

^aActual (measured) polymer coating volumes of the SPME fibers are presented in Jonker et al. (2018). SPME = solid-phase micro-extraction.

air-dried polymer pieces were stored in solvent-rinsed 20-ml vials. Fibers were stored in 20-ml vials containing Milli-Q water. Storing lasted for 2 weeks at most.

Experimental determination of polymer–water partitioning

Polymer–water partition coefficients for all polymers were determined in fivefold (five replicates) as described before (Jonker et al., 2015). Briefly, samplers were added to ultraclean 250-ml amber-colored glass bottles, followed by the addition of Milli-Q water containing 100 mg/L of sodium azide. The bottles were then spiked, closed with glass stoppers, and shaken at 150 rpm and 20 °C in the dark for 12 weeks. After the equilibration period, the water phases were sampled and liquid–liquid extracted with *n*-hexane, after which the samplers were collected and extracted in autosampler vials containing acetonitrile. Modifications as compared with the previous study (Jonker et al., 2015) were (1) the systems were spiked with 15–80 μl of a cocktail solution of PAHs and PCBs in acetone (~5 mg/L PCBs, 1.5 or 3 mg/L PAHs; see the Supporting Information, Table S1); (2) when the equilibration ended, some polyethylene samplers (PE-1 and -2) appeared to float on the water surface and were sampled first, before sampling the water phase; (3) liquid–liquid water phase extraction recovery and blank determinations were performed in five replicates; (4) the extraction volume for samplers was tuned to the expected concentrations and varied between 0.2 ml (S10 and S30 fibers) and 1.5 ml (polyethylene); and (5) vortexing (extracting) the samplers lasted for 1 min (fibers) or 4 min (sheet samplers). Chemical analysis of PAHs and PCBs was performed as described before as well (Jonker et al., 2015). Polymer–water partition coefficients were finally obtained by dividing the concentrations in the samplers (as calculated from the concentrations in the sampler extracts and the sampler masses) by the concentrations in the water phases (as calculated from the blank- and recovery-corrected concentrations in the water phase extracts and the extracted water masses). Water phase

extraction recoveries were 99% ± 1%, and overall mass balances of the partition experiments measured 96% ± 4% (average of all chemicals and systems). Equilibrium conditions were checked by comparing the results for different samplers of the same polymer, having different thicknesses.

Polymer–polymer partitioning

To investigate any differences in PAH and PCB affinity for the different materials in detail, a dedicated polymer–polymer partitioning experiment was performed. This experiment was used solely to compare samplers mutually. Water phases were not sampled, and thus actual K_{p-w} values were not determined. Thin strings were cut from a silicone rubber sheet (AlteSil translucent; Altec Extrusions; thickness 500 μm) and Soxhlet-extracted with ethyl acetate for 100 h. The strings were air-dried and cut into granules of approximately 0.5 mm³ with a razor blade. Approximately 1 g of granules was transferred into eight preweighed 25-ml full-glass bottles, using acetone and a glass funnel. The acetone was decanted, and the granules were washed in the bottles with methanol (2 × 30 min shaking at 200 rpm), after which the bottles were placed under an N₂ flow to evaporate the remaining methanol and weighed to determine the exact silicone rubber mass. Then 23 ml of methanol/water (50/50 v/v) and 400 μl of a PAH/PCB spike (10/20 mg/L in acetone) were added to each bottle, after which the bottles were closed with glass stoppers and shaken for 4 weeks at 180 rpm. The liquid phases were then removed with a pipette, and the bottle contents were washed with Milli-Q water (3 × 30 min). Finally, 23 ml of Milli-Q water, containing 100 mg NaN₃/L, and three polyethylene samplers with different shapes (such that they could be distinguished) and a known weight (approximately 3.5 mg each) were added to each system. The bottles were closed and placed on a reciprocal shaker at 180 rpm and 20 ± 1 °C for 12 weeks. A pilot kinetic experiment had demonstrated that all spiked PAHs and PCBs equilibrated with the polyethylene samplers within 6 weeks in this setup (see the Supporting Information, Figure S1).

This experiment focused on polyethylene, because another pilot experiment had shown that the silicone rubber dosing granules became tightly stuck to the PDMS samplers, in particular the SSP sheet samplers, and it was impossible to separate them. In addition, 10- and 30- μm PDMS-coated fibers appeared to break during the shaking, which further complicated a full recovery of the fibers. Still, to one quadruplicate system, 5-cm-long pieces of the more robust 100- μm PDMS-coated fiber (S100) were added.

Following the equilibration period, samplers were harvested from the bottles, dried by wiping with tissue, and placed in autosampler vials containing acetonitrile. Internal standards were added to the vials, and they were left for a day, after which they were vortexed for 4 min.

Literature K_{p-w} data compilation

Experimentally determined polyethylene–water (K_{PE-w}) and PDMS–water (K_{PDMS-w}) partition coefficients for PAHs and PCBs were collected from the scientific literature published up until mid-2021. In contrast to previous data compilations and comparisons (see Bao et al., 2012; DiFilippo & Eganhouse, 2010; Hale et al., 2010; Lohmann, 2012; Reitsma et al., 2013; Smedes et al., 2009; Zhu et al., 2015), in which all available data were included, the present compilation only includes coefficients determined under “standard conditions,” that is, in freshwater (salinity less than 0.5 ppt) at $20 \pm 2^\circ\text{C}$ (Jonker et al., 2015). After all, polymer–water partitioning is dependent on temperature (Booij et al., 2003; Jonker et al., 2015; Muijs & Jonker, 2009) and salinity (Jonker & Muijs, 2010; Jonker et al., 2015), and coefficients determined at different temperatures or salinities should therefore not be pooled. Thus K_{PE-w} and K_{PDMS-w} values resulting from seawater exposures (Lee et al., 2014; Perron et al., 2009; Reitsma et al., 2013; Zeng et al., 2005) or experiments performed at lower (Booij et al., 2003; Reitsma et al., 2013) or higher temperatures (Adams et al., 2007; Booij et al., 2003; Eganhouse, 2016; Grant et al., 2016; Hsieh et al., 2011; Lee et al., 2014; Mayer et al., 2000; Paschke & Popp, 2003; Yang et al., 2007; Zhu et al., 2015) were excluded from the database. The temperature range of $20 \pm 2^\circ\text{C}$ was selected because it matches with the exposure temperature applied in the majority of (high-quality) literature studies and the present study, as well as with the exposure temperature defined in the recently published passive sampling standard protocol (Jonker et al., 2020).

Selection of best available partition coefficients

The overall goal of the present study was to select and propose best available K_{PE-w} and K_{PDMS-w} values for PAHs and PCBs. The following criteria were used for the selection: The best available values should (1) be experimentally determined at standard conditions, and thus be part of the present data compilation or experimental results; (2) be determined according to a reliable, high-quality experimental setup; (3) have high precision, that is, low standard deviations (preferably less

than 0.1 log unit); (4) be part of a “larger” data set, that is, not be just one of few (less than 5) values determined in a single study, such as to be able to judge the mutual relationship with other chemicals of the same chemical group (PAHs or PCBs) and with hydrophobicity; and (5) display a clear linear and tight log–log correlation with K_{OW} . Any leveling-off or cut-off in this relationship points to the occurrence of artifacts caused by test chemical precipitation, the presence of a “third phase,” or nonequilibrium conditions (Jonker & van der Heijden, 2007; Jonker et al., 2015) and thus would require rejection of the data. The K_{OW} values used for assessing the last criterion are presented in the Supporting Information, Table S2. They concern experimentally determined slow stirring values for PAHs (Jonker, 2016) and slow stirring/modeled values for PCBs (Sabljić et al., 1993).

RESULTS AND DISCUSSION

Literature K_{PE-w} and K_{PDMS-w} database

K_{PE-w} values reported in the scientific literature were previously collected and reviewed by Lohmann in 2012. Based on his compilation, Lohmann proposed “best fit” K_{PE-w} values for selected PAHs and PCBs. Since the publication of that review, additional K_{PE-w} values have become available: eight studies were published with K_{PE-w} values for PAHs and three with data for PCBs. However, some of these additional studies, as well as some already included by Lohmann (2012), reported K_{PE-w} values determined at conditions other than those specified in the present study as “standard conditions” (i.e., freshwater of $20 \pm 2^\circ\text{C}$). As mentioned in the *Materials and Methods* section, data from these studies (Adams et al., 2007; Booij et al., 2003; Lee et al., 2014; Perron et al., 2009; Zhu et al., 2015) were excluded from the present database. As a result, the present database contains K_{PE-w} values from 10 studies for PAHs (Supporting Information, Table S3A) and from 4 studies for PCBs (Supporting Information, Table S3B). Metadata of the included studies (i.e., information on samplers and experimental conditions) are presented in the Supporting Information, Table S3C. Minimum and maximum chemical-specific K_{PE-w} values and the range covered, expressed as a factor, are given in the Supporting Information, Tables S3A and B.

The PAH data set in particular demonstrated a high degree of variability: chemical-specific K_{PE-w} values differed by as much as a factor of up to 66. For PCBs, the variability was less, with the data up to PCB-137 agreeing within a factor of three. For PCBs higher than PCB-137, the variability increased up to a factor of 17. The data variability is illustrated in Figure 1A and B, in which the K_{PE-w} values are plotted against K_{OW} values (open symbols). Because effects of temperature and salinity are excluded, the observed variability probably primarily illustrates the experimental difficulties in determining K_{PE-w} for hydrophobic chemicals (i.e., the interlaboratory variability) and thereby clearly stresses the need for standard values. However, part of the observed variability may also be due to differences in sorption capacities of the different polyethylene batches used in the various studies. This aspect, as well as the selection

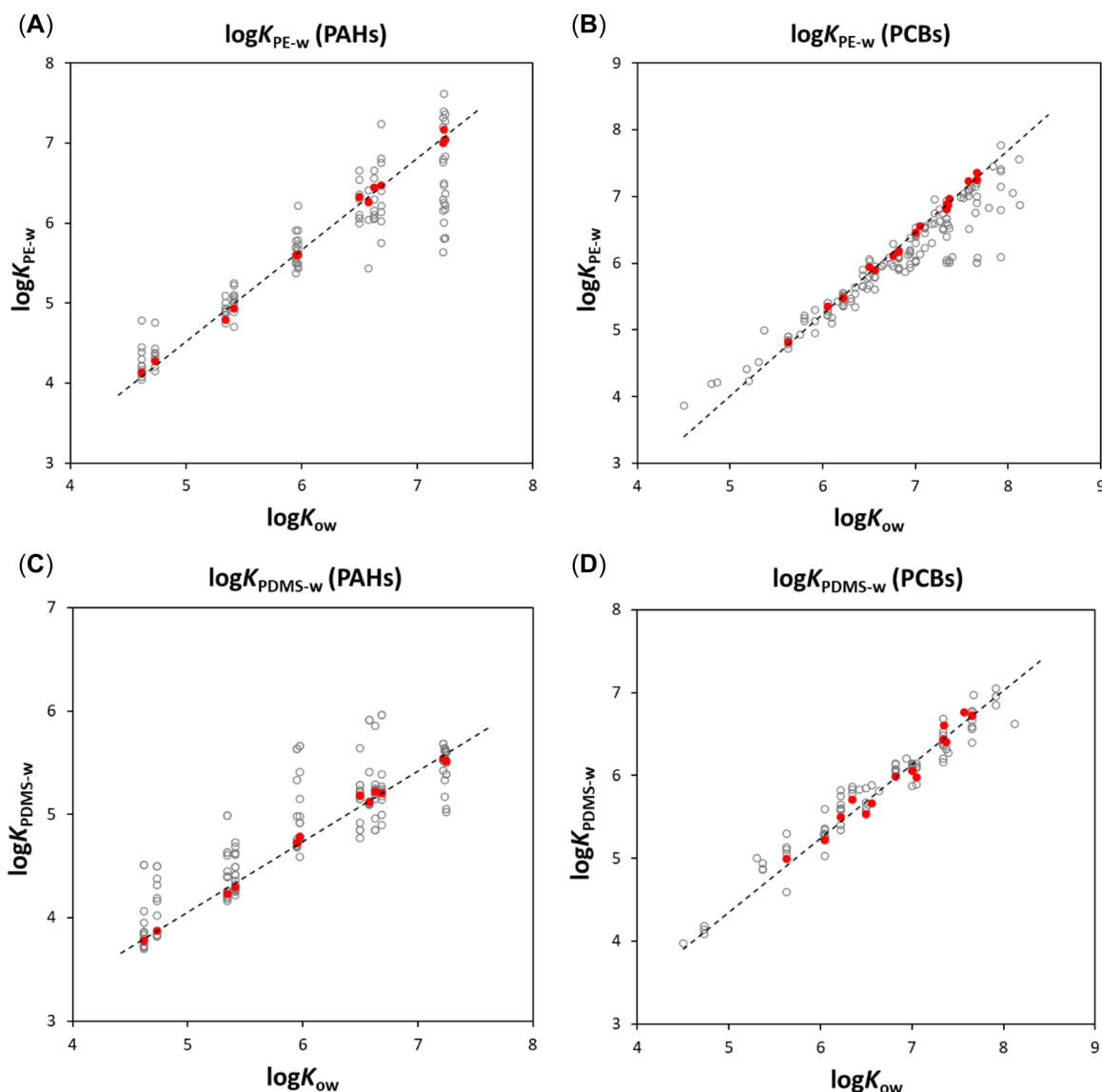


FIGURE 1: Relationships between $\log K_{p-w}$ and $\log K_{ow}$. Open gray markers represent literature values (Supporting Information, Tables S3 and S4). Solid red markers represent (averaged) values determined in the present study. Dashed lines are regression lines for the latter data. Data for polyethylene (PE) are presented in (A) (polycyclic aromatic hydrocarbons [PAHs]) and (B) (polychlorinated biphenyls [PCBs]); data for polydimethylsiloxane (PDMS) are shown in (C) (PAHs) and (D) (PCBs).

of best available values, will be discussed in the following sections.

K_{PDMS-w} values were compiled and reviewed by DiFilippo and Eganhouse in 2010. Their database contains K_{PDMS-w} values for various temperatures, salinities, and sampler thicknesses and suppliers, as well as values relating to PDMS and “more complicated” silicone rubbers. Even after these authors excluded data that did not pass their own quality criteria, the observed variability was very large, more than 2 orders of magnitude for PCBs. Preferred or “best fit” K_{PDMS-w} values were not selected by the authors. In the present database, K_{PDMS-w} values determined at “nonstandard conditions” were not included. In addition, data for silicone rubbers other than PDMS were omitted, because these polymers can have sorption characteristics different from those of PDMS (Jonker et al., 2015) and different mutual sorption characteristics

(Smedes et al., 2009). The resulting cleaned-up database was supplemented with K_{PDMS-w} data obtained at standard conditions and published between 2010 and mid-2021, that is, data from four studies for PAHs and two studies for PCBs. The final compilation is presented in the Supporting Information, Table S4A–C and contains 18 PAH data sets from 15 literature sources (Supporting Information, Table S4A) and 7 PCB data sets from 5 literature sources (Supporting Information, Table S4B). Although this database contains PCB data from more studies compared with the K_{PE-w} database (Supporting Information, Table S3B), the number of included PCB congeners is less than half the number of congeners in the Supporting Information, Table S3B. The range in K_{PDMS-w} values (i.e., the factors in the Supporting Information, Table S4A and B) is smaller than that observed for polyethylene: K_{PDMS-w} values for PCBs match within a factor of 4 for all congeners and

within a factor of 12 for PAHs. Although still substantial, this range is also much smaller than that observed in the 2010 database (DiFilippo & Eganhouse, 2010). This may again illustrate the challenging nature of K_{p-w} determinations or the influence of temperature and salinity, but in this case also the differences between silicone rubbers and PDMS. The data variability is illustrated in Figure 1C and D. Whether this variability is exclusively caused by interlaboratory differences or whether differences in sampler sorption capacities may have contributed is explored in the later section, *New experimental K_{PDMS-w} values: Effect of polymer source.*

New experimental K_{PE-w} values: Effect of polymer source

In the present study, K_{PE-w} values were determined for six polyethylene samplers with different sources and thicknesses (Table 1). The results are presented in the Supporting Information, Table S5. Generally, the measurements were performed with high precision: standard deviations of the K_{PE-w} values were less than 0.1 log units in the majority of cases. Exceptions were the high-molecular-weight compound data for the PE-1 and -2 samplers, which deviated from the K_{PE-w} values obtained for the other samplers and showed some leveling-off and increased variability with hydrophobicity (gray values in the Supporting Information, Table S5). Typically, such behavior points to nonequilibrium conditions (Jonker & Van der Heijden, 2007; Jonker et al., 2015). However, these conditions seem illogical in the present study, because the log K_{PE-w} values for PE-3 and -4/5/6, that is, samplers having different thicknesses (51 vs. 25 μm), were very similar and did not show any leveling-off, which indicates equilibrium conditions for these samplers. Moreover, all six polyethylene samplers were equilibrated simultaneously in the same way and for the same length of time. Still, experimental observations may actually support the nonequilibrium hypothesis for PE-1 and -2: when the shaking ended, just before sampling of the water and polymer phases, these samplers floated up to the water surface, in contrast to the other polyethylene samplers, which stayed submerged. Most probably, this behavior is linked to the density of the samplers and will have had consequences for the hydrodynamics in the system (Jonker et al., 2015). Samplers with a lower density will move along with the water current more than those with a higher density, resulting in an increased thickness of the aqueous boundary layer surrounding the first samplers and thus slower equilibration kinetics (and increased data variability) of the more hydrophobic compounds in particular. One way of dealing with such behavior is to fix the sampler on a small rod placed inside the bottle (Booij et al., 2017).

To test this hypothesis and to investigate whether PE-1 and -2 differed from the other polyethylene samplers in terms of sorption characteristics, an additional polymer–polymer partitioning experiment was performed (see *Materials and Methods*). In contrast to the approach applied by Gilbert et al. (2016), the different polyethylene samplers were equilibrated with each other in water, excluding potential effects of

(residual) solvent (Gilbert et al., 2016; Smedes, 2019). The results of this experiment are presented in the Supporting Information, Tables S6 and S7, and show that the sorption capacity of the PE-1 and -2 samplers for the more hydrophobic compounds was not reduced compared with that of the other polyethylenes. Hence, the deviating K_{PE-w} values of PE-1 and -2 in the Supporting Information, Table S5 would have been caused by an artifact, that is, nonequilibrium conditions, most probably due to poor hydrodynamics; thus these values were excluded from further data analysis. The presence of artifacts once more clearly illustrates the challenging nature of K_{p-w} determinations for hydrophobic chemicals (Booij et al., 2016; Jonker et al., 2015). Note that the Supporting Information, Table S6, presents concentration ratios between 25- and 51 μm -thick samplers. The observed similar ratios therefore indicate equilibrium conditions in this additional experiment.

Another conclusion that can be drawn from the Supporting Information, Table S6, is that, although comparable, the sorption capacities of the different polyethylene samplers were not equal. Compared with PE-3 as a reference, being the thickest sampler, (1) the sorption capacity of PE-1 for PAHs increased with hydrophobicity by up to approximately 20%, whereas the sorption capacity for PCBs was approximately 15% higher, independent of hydrophobicity; (2) the sorption capacity of PE-2 for PAHs increased with hydrophobicity by up to approximately 15%, whereas the sorption capacity for PCBs was the same; (3) the sorption capacity of PE-4 for both compound groups was approximately 20%–30% higher; and (4) the sorption capacity of PE-5 for PAHs increased with hydrophobicity by up to approximately 30%, whereas the sorption capacity for PCBs was approximately 10% higher, independent of hydrophobicity. Most of these differences were significant (analysis of variance, two-factor with replication; $\alpha = 0.05$; Microsoft Excel), implying that the sorption capacities of the presently investigated polyethylene batches were significantly different, up to approximately 30%. In addition, different polyethylene batches from the same supplier could differ: PE-2 and -5 are both from Berry Global, but they differed slightly in their sorption properties. (Note that PE-5 is specified as “Film-Gard.”) The differences in sorption capacities between the different polyethylenes translated into differences in log K_{PE-w} values of up to approximately 0.1 log unit (Supporting Information, Table S7). Some of these differences were more or less reflected by the actual log K_{PE-w} values (see the Supporting Information, Table S5 and Figure S2), such as the systematically stronger partitioning of all compounds to PE-4. However, other differences were lost in the data variability, that is, the standard deviations of the actual log K_{PE-w} values in the Supporting Information, Table S5. Still, and even though the differences are not clearly visible when the results are compared graphically (Figure 2A), it is concluded that different polyethylene batches can have significantly different log K_{PE-w} values. When polyethylene is used as a passive sampler, application of fixed, batch-independent log K_{PE-w} values may thus lead to inaccurate C_{free} values. These may be up to 30% off the true value, although higher percentages cannot be excluded for other, not yet investigated, polyethylene batches. For this

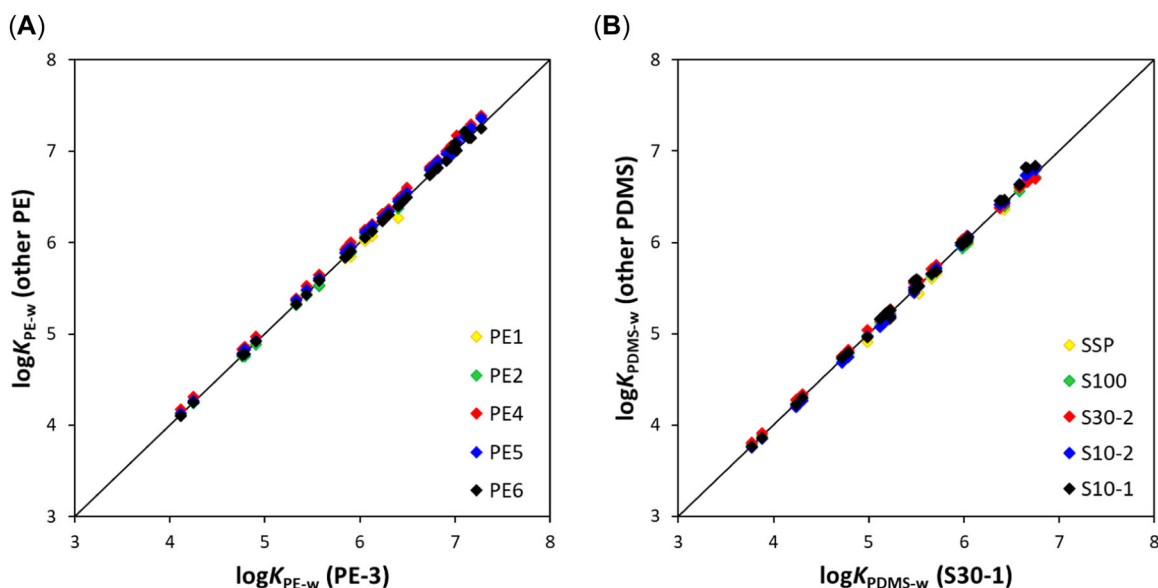


FIGURE 2: Mutual comparison of polycyclic aromatic hydrocarbon and polychlorinated biphenyl partitioning to different samplers of the same type of polymer. (A) $\log K_{PE-w}$ values for polyethylene (PE)-1, 2, 4, 5, and 6 versus $\log K_{PE-w}$ values for PE-3. Biased values for PE-1 and -2 (see the Supporting Information, Table S5, and main text for explanation) are excluded. (B) $\log K_{PDMS-w}$ values for S10-1, S10-2, S30-2, S100, and SSP versus $\log K_{PDMS-w}$ values for S30-1. For an explanation of sampler codes, see Table 1. PDMS = polydimethylsiloxane.

reason, the $\log K_{PE-w}$ values in the Supporting Information, Table S5, basically should not be averaged, which challenges the determination of best available values (discussed further in the *Best available partition coefficients* section).

The cause of the intersource variation in $\log K_{PE-w}$ will most probably be related to the presence of additives or filling materials in the polymers (Lohmann, 2012) or the degree of polymer branching. On the one hand, the addition of fillers could reduce sorption to the polymer. On the other hand, known fillers such as soot or silica gel (Lohmann, 2012) could explain the increased sorption with increasing hydrophobicity and the number of rings observed exclusively for PAHs in PE-5, -1, and -2, compared with PE-3 and -6 (Jonker & Koelmans, 2002). Interestingly, although this phenomenon did not clearly occur with PE-4, increased partitioning of the co-planar PCBs (77, 126, 169) to this polyethylene sheet was observed (Supporting Information, Table S6), which could suggest the presence of an additive or filler that can preferentially bind planar chemicals (Jonker & Koelmans, 2002) in this polyethylene as well. Still, this polyethylene sheet and PE-6 in particular were clearly transparent, whereas the other polyethylene sheets were blurred or whitish.

New experimental K_{PDMS-w} values: Effect of polymer source

Experimental K_{PDMS-w} values were determined for six PDMS-based samplers from different suppliers and with different thicknesses. The resulting sampler-specific values are reported in the Supporting Information, Table S8. Again, the measurements appeared to be of high precision, because standard deviations were generally less than 0.1 log unit for these samplers as well; however, there were two exceptions. First, the data for dibenz[*a,h*]anthracene suffered from increased

intra- and intersampler variability, and the values obtained were obviously too low. Increased intrasampler variability (low precision) for this chemical has been observed before (Jonker & Muijs, 2010; Muijs & Jonker, 2009) and probably is due to the chemical's extremely low aqueous solubility. After spiking, precipitation may occur and because of the slow dissolution kinetics of the precipitates (Jonker et al., 2015), this may finally result in variable nonequilibrium conditions. If the precipitates are included in the water phase sampling and extraction, K_{PDMS-w} values that are too low will be the result. The reason why this effect was observed for PDMS, but not for polyethylene is unclear, all the more so because spike loadings for polyethylene were approximately a factor of 4 higher than for PDMS and extreme care was taken to avoid any artifacts. Second, for the PDMS sheet (from SSP), a similar effect was also observed for the other two 6-ring PAHs benzo[*ghi*]perylene and indeno[123-*cd*]pyrene, as well as for the six most hydrophobic PCBs. Because this effect resembles that observed for PE-1 and -2, nonequilibrium conditions are plausible here as well. In this case, they could be related to poorer hydrodynamics of the freely moving sheet samplers compared with the higher density (glass core) and thus less mobile SPME fibers. Unfortunately, this hypothesis could not be tested with the polymer–polymer partitioning setup, because of reasons explained in *Materials and Methods*, but a recently published data set on SSP sheets (Smedes, 2019) confirms the absence of a cut-off effect for this sheet sampler (Supporting Information, Table S4A–C). The polymer–polymer setup was used, however, to validate the K_{PDMS-w} values for the S100 fiber. This fiber was added in the setup, and by using K_{PE-w} values from the Supporting Information, Table S5, and measured concentrations in polyethylene and S100, K_{PDMS-w} values were calculated. These values (results not shown) matched those listed in the

Supporting Information, Table S8, within 0.03 log units for all PAHs, except for benzo[ghi]perylene, for which the value was 0.06 log units higher. Because this approach also yielded a value for dibenz[a,h]anthracene, which was according to expectations based on previous values (Jonker & Van der Heijden, 2007; Jonker, 2016; Muijs & Jonker, 2009), as an exception, this value was taken as substitute for the biased value obtained in the batch shake setup.

Although polymer–polymer partitioning measurements were not performed for PDMS, the results in the Supporting Information, Table S8 and Figure S3, demonstrate that there were no obvious systematic differences between the different PDMS samplers. Standard deviation intervals overlapped in the vast majority of cases, excluding the biased SSP sheet data for high-molecular-weight compounds. This implies that (1) equilibrium conditions were attained for all the SPME fiber samplers, with different coating thicknesses, and (2) the different PDMS samplers investigated in the present study, which were obtained from different sources, had identical sorption capacities. Therefore, chemical-specific $K_{\text{PDMS-w}}$ values for the different samplers were averaged, after excluding the biased values for SSP sheets and taking the value for dibenz[a,h]anthracene derived in the polymer–polymer partitioning experiment (see the Supporting Information, Table S8). The identical sorption characteristics of the various PDMS samplers are illustrated in Figure 2B.

Proposed best available partition coefficients

To substantiate the selection of best available $K_{\text{p-w}}$ values, the data sets included in the present literature database were scored according to several criteria (see *Materials and Methods*). The results of the scoring process are presented in the Supporting Information, Tables S9 ($K_{\text{PE-w}}$) and S10 ($K_{\text{PDMS-w}}$). To allow assessment of the last selection criterion, that is, judging equilibrium conditions and any precipitation or “third phase” artifacts, $\log K_{\text{ow}} - \log K_{\text{p-w}}$ plots were constructed, which are presented in the Supporting Information, Figures S4 ($K_{\text{PE-w}}$) and S5 ($K_{\text{PDMS-w}}$). Most data sets did not have a maximum score and did not, or only to a limited extent, qualify as best available data set. Obviously, for polyethylene the situation is the most complicated, because $K_{\text{PE-w}}$ values can be dependent on the polyethylene batch (producer, supplier). Therefore, proposing best available $K_{\text{PE-w}}$ values is basically impossible without standardizing the polyethylene material. Hence, it is proposed that future polyethylene sampling experiments by the passive sampling community be performed with polyethylene obtained from either Brentwood Plastics (PE-3) or VWR International (PE-6). These polyethylene sheets have identical sorption properties for PAHs and PCBs, but different thicknesses, thereby offering optionality in kinetic properties and sensitivity and allowing verification of equilibrium conditions based on the application of sheets of different thicknesses (Jonker et al., 2020), all by using a single set of $K_{\text{PE-w}}$ values. Note that these particular sheet versions have been proposed as sampling materials in the recently published passive sampling standard protocol as well

(Jonker et al., 2020). Proposing these materials as standard samplers implies that the $K_{\text{PE-w}}$ values for PE-3 and -6, as obtained in the present study, are the most logical candidates for best available values. Although this nomination may seem subjective, it is a legitimate choice considering the scores of the present data set (Supporting Information, Table S7). The only other possible candidates are the data sets by Choi et al. (2013), Fernandez et al. (2009), and Smedes et al. (2009). However, a comparison of these sets with the present data set (averaged values of PE-3 and -6; verified equilibrium conditions) suggests that the first two sets are biased for the high-molecular-weight compounds, considering the downward curvatures in the Supporting Information, Figure S6A and B, the first most notably for PAHs, for which values differed from the present values by up to 0.82 log units, and the second for PCBs, showing differences of up to 0.48 log units. The data set by Smedes et al. (2009) matches the present data set well for PCBs, but values for the PAHs deviate by up to 0.36 log units (Supporting Information, Figure S6C). Smedes et al. (2009) used a sheet obtained from Brentwood as well (like PE-3), but it had a different thickness (70 μm) and was purchased several years before the present one. Hence, the possibility cannot be excluded that the materials had different compositions, for instance because the company changed the production process over the years. All in all, it is proposed that the present data set qualifies best as the best available $K_{\text{PE-w}}$ set, all the more so because the systematically higher values for PAHs in the Smedes et al. (2009) data set were not observed, at least not for the first six PAHs, by Choi et al. (2013), who applied the exact same material as used in the present study (PE-3 was kindly donated by Y. Choi). Also, this effect was not observed for PAH partitioning to SSP sheets (Smedes, 2019), as will be discussed later. This seems to rule out any systematic inter-laboratory differences between the results of the Smedes and the present laboratory, which is supported by the fact that the averaged difference in the results of both laboratories when analyzing PAH standards during the recent interlaboratory comparison study (Jonker et al., 2018) was only 7%. Therefore, $K_{\text{PE-w}}$ values for PE-3 and -6 were averaged and are listed in Table 2 as proposed best available values. The relationship between these values and the literature data is illustrated in Figure 1A and B. Because the present PCB data set is relatively small (18 congeners) and the PCB data by Smedes et al. (2009) agree very well with the present data (based on the mutually tested congeners), the PCB data set in Table 2 was expanded by supplementing with data for additional PCBs from the Smedes et al. data set. As a result, 44 best available PCB $K_{\text{PE-w}}$ values are listed in Table 2.

The overall resulting proposed best available $K_{\text{PE-w}}$ data set agrees reasonably, but not very well with the best fit values from Lohmann (2012; see Supporting Information, Figure S7). Differences between the two data sets of up to 0.47 log units are observed. It should be noted, however, that the values proposed by Lohmann (2012) represent calculated, one decimal values, which were modeled based on a QSPR that was fitted to pooled data originating from different studies using different polyethylene sources and exposure temperatures, as

TABLE 2: Proposed best available log K_{PE-w} and log K_{PDMS-w} values for polycyclic aromatic hydrocarbons^a and polychlorinated biphenyls^b

	Log K_{PE-w}	Log K_{PDMS-w}
Phenanthrene	4.11 (±0.01)	3.78 (±0.03)
Anthracene	4.25 (±0.01)	3.87 (±0.04)
Fluoranthene	4.77 (±0.01)	4.23 (±0.04)
Pyrene	4.91 (±0.01)	4.30 (±0.03)
Benz[a]anthracene	5.58 (±0.01)	4.78 (±0.04)
Chrysene	5.58 (±0.01)	4.72 (±0.03)
Benzo[e]pyrene	6.24 (±0.03)	5.12 (±0.04)
Benzo[b]fluoranthene	6.30 (±0.03)	5.18 (±0.04)
Benzo[k]fluoranthene	6.42 (±0.04)	5.22 (±0.05)
Benzo[a]pyrene	6.44 (±0.04)	5.21 (±0.04)
Benzo[ghi]perylene	7.03 (±0.07)	5.51 (±0.09)
Dibenz[a,h]anthracene	6.99 (±0.08)	5.54 (±0.08)
Indeno[123,cd]pyrene	7.15 (±0.09)	5.54 (±0.08)
PCB-1 ^c		4.04 (±0.04)
PCB-2 ^c		4.18 (±0.04)
PCB-3 ^c		4.15 (±0.03)
PCB-4 ^c	4.19 (±0.12)	4.20 (±0.19)
PCB-10 ^c	4.23 (±0.12)	4.35 (±0.08)
PCB-14 ^c	4.99 (±0.11)	4.81 (±0.05)
PCB-18 ^d	4.78 (±0.01)	4.97 (±0.05)
PCB-21 ^c	5.22 (±0.11)	5.14 (±0.06)
PCB-28 ^d	5.33 (±0.01)	5.20 (±0.05)
PCB-29 ^c	5.31 (±0.07)	5.19 (±0.07)
PCB-30 ^c	5.13 (±0.09)	5.01 (±0.04)
PCB-31 ^c	5.30 (±0.10)	5.18 (±0.09)
PCB-44 ^c	5.48 (±0.10)	5.49 (±0.08)
PCB-47 ^c	5.62 (±0.10)	
PCB-49 ^c	5.67 (±0.10)	5.58 (±0.08)
PCB-50 ^c	5.52 (±0.09)	5.43 (±0.06)
PCB-52 ^d	5.43 (±0.01)	5.49 (±0.05)
PCB-55 ^c	5.82 (±0.09)	5.73 (±0.07)
PCB-56 ^c	5.90 (±0.09)	
PCB-66 ^d	5.84 (±0.02)	5.65 (±0.04)
PCB-72 ^d	5.86 (±0.02)	5.70 (±0.04)
PCB-77 ^d	5.91 (±0.02)	5.52 (±0.06)
PCB-78 ^c	6.03 (±0.08)	5.69 (±0.05)
PCB-81 ^c		5.75 (±0.14)
PCB-85 ^c	6.14 (±0.13)	
PCB-87 ^c	6.18 (±0.09)	
PCB-97 ^c	6.10 (±0.06)	
PCB-99 ^c	6.38 (±0.06)	
PCB-101 ^d	6.13 (±0.02)	5.98 (±0.04)
PCB-103 ^d	6.05 (±0.02)	6.02 (±0.04)
PCB-104 ^c	6.00 (±0.08)	5.88 (±0.07)
PCB-105 ^c	6.44 (±0.08)	6.11 (±0.08)
PCB-110 ^c	6.16 (±0.09)	
PCB-114 ^c		6.07 (±0.15)
PCB-118 ^d	6.40 (±0.03)	6.04 (±0.05)
PCB-123 ^c		6.03 (±0.11)
PCB-126 ^d	6.50 (±0.04)	5.98 (±0.04)
PCB-128 ^c	6.74 (±0.07)	
PCB-137 ^c	6.93 (±0.05)	
PCB-138 ^d	6.74 (±0.06)	6.41 (±0.06)
PCB-141 ^c	6.74 (±0.09)	
PCB-145 ^c	6.52 (±0.07)	6.44 (±0.04)
PCB-149 ^c	6.59 (±0.08)	
PCB-151 ^c	6.55 (±0.10)	
PCB-153 ^d	6.82 (±0.06)	6.42 (±0.06)
PCB-155 ^d	6.81 (±0.06)	6.60 (±0.05)
PCB-156 ^d	6.90 (±0.07)	6.41 (±0.07)
PCB-157 ^c		6.48 (±0.10)
PCB-167 ^c		6.47 (±0.14)
PCB-169 ^d	7.01 (±0.10)	6.32 (±0.08)

(Continued)

TABLE 2: (Continued)

	Log K_{PE-w}	Log K_{PDMS-w}
PCB-170 ^d	7.16 (±0.12)	6.72 (±0.11)
PCB-180 ^d	7.26 (±0.11)	6.73 (±0.10)
PCB-187 ^d	7.15 (±0.10)	6.76 (±0.09)
PCB-189 ^c		6.92 (±0.15)
PCB-204 ^c	7.77 (±0.33)	7.43 (±0.12)

^aData for PAHs are from the present study. Values in parentheses are standard deviations of replicated batch-shake measurements.^bNote that several PCB congeners do not occur in the environment, but are only applied as performance reference compounds (PCBs 1, 2, 3, 4, 10, 14, 21, 29, 30, 50, 55, 78, 104, 145, 155, and 204).^cPCB data for PE are from Smedes et al. (2009). Values in parentheses are 95% confidence intervals of the log K_{PE-w} values obtained by extrapolation of co-solvent curves. Data for PDMS are from Smedes (2019). Values in parentheses are standard errors obtained by error propagation as described in Smedes (2019).^dPCB data from the present study. Values in parentheses are standard deviations of replicated batch-shake measurements.

PAH = polycyclic aromatic hydrocarbon; PCB = polychlorinated biphenyl; PDMS = polydimethylsiloxane; PE = polyethylene.

well as salinity-corrected data from seawater experiments. In this respect, it should be stressed that application of the K_{PE-w} values from Table 2 to polyethylene from other sources, or to exposures under nonstandard conditions, may lead to erroneous C_{free} results. For instance, application to polyethylene from Covalence Plastics (PE-4) will result in a systematic 20%–30% overestimation of C_{free} . Therefore, when one is using this polyethylene, application of the K_{PE-w} values from Table 2 is discouraged, unless measurement goals allow the deviations in C_{free} . Instead, the batch-specific K_{PE-w} values obtained for this polyethylene (Supporting Information, Table S5) could be applied. For polyethylene from sources not included in the present study, batch-specific K_{PE-w} values could relatively easily be determined by applying the polymer–polymer setup described in the present study, using PE-3 or -6 as a reference phase.

For PDMS, more data sets qualify as best available data set. These primarily concern PAH data, as obtained by Muijs and Jonker (2009), Jonker et al. (Jonker & Muijs, 2010; Jonker & Van der Heijden, 2007; Jonker, 2016), Ter Laak et al. (2006), and Smedes (2019), which all agree very well with the values obtained in the present study (excluding one biased value for dibenz[a,h]anthracene from Jonker and Muijs [2010]). Averaging these literature and the present data yields K_{PDMS-w} values that agree with the data obtained in the present study within 0.05 log units for benzo[ghi]perylene and indeno[123,cd]pyrene and within 0.00–0.03 log units for all other PAHs. Because the observed differences are marginal and within the measurement uncertainty, and averaging data from multiple sources does not allow for meaningful standard deviations, it is proposed to use the K_{PDMS-w} values determined in the present study as best available values. These values represent robust and consistent data, showing no systematic differences between six different PDMS samplers (barring the exceptions discussed). Hence, the averaged PAH values from the Supporting Information, Table S8, were included in Table 2. The only literature data set that qualifies as best available set for PCBs is the one by Smedes (2019). This data set also agrees

very well with the present data set (see the Supporting Information, Figure S8), but it was obtained through an indirect approach. Therefore, for PCBs also, the presently obtained $K_{\text{PDMS-w}}$ values can be considered the most logical candidates for best available values. However, analogous to the polyethylene case, the list with 18 PCB $K_{\text{PDMS-w}}$ values from the present study was supplemented with values for additional PCB congeners from the Smedes (2019) list. Consequently, Table 2 presents $K_{\text{PDMS-w}}$ values for 42 PCBs. It should be stressed once more that these values apply to PDMS, that is, the polymer present as the coating on SPME fibers from Polymicro Technologies and Fiberguide Industries and the polymer used for the production of sheets by SSP, and thus should not be applied to “more complicated” silicone rubbers. The latter polymers can have deviating sorption characteristics, as was demonstrated before (Smedes et al., 2009) and is illustrated for a specific silicone rubber in the Supporting Information, Figure S9. The proposed $K_{\text{PDMS-w}}$ values in Table 2 do not all match well with values calculated based on the $\log K_{\text{ow}} - \log K_{\text{PDMS-w}}$ QSPRs derived by DiFilippo and Eganhouse (2010) and Ghosh et al. (2014; see the Supporting Information, Figure S10). Applying the first model, values for PAHs are overestimated by up to 0.57 log units, whereas values for PCBs are underestimated by up to 0.79 log units. It should be noted, however, that this QSPR was derived based on partitioning data for a broad range of chemicals using PDMS and silicone rubbers at different temperatures and salinities. In contrast, the second QSPR considerably overestimates values for PCBs (by up to 0.74 log units), whereas values for PAHs are predicted relatively well (within 0.22 log units).

The $K_{\text{PE-w}}$ and $K_{\text{PDMS-w}}$ data presented in Table 2 were selected based on a quality assessment of experimental data obtained by various research groups over the course of two decades of research on polymer–water partitioning of hydrophobic organic chemicals and presumably represent the presently best available data in this field. Therefore, the passive sampling community is encouraged to use this data set. Universal use of these proposed values, in combination with the application of standard protocols (Jonker et al., 2020), will improve the accuracy of C_{free} determinations and enable a straightforward comparison of results across different laboratories worldwide (Jonker et al., 2018). Admittedly, the proposed data set in Table 2 relates to rather narrow exposure conditions (freshwater; 20 ± 2 °C). Hence, the set is applicable to passive sampling activities performed under these conditions, such as ex situ passive sampling in the laboratory (Jonker et al., 2020). Calculation of C_{free} based on passive sampling at other temperatures or salinities, for example, in the field, would require temperature and salinity corrections to the coefficients (Jonker et al., 2015). Such corrections were outside the scope of the present study, but may be the topic of future research. Finally, Table 2 lists $\log K_{\text{p-w}}$ values for only a limited number of chemicals. $\log K_{\text{p-w}}$ values for PAHs or PCB congeners not included in Table 2 could, if needed, be estimated by using QSPRs obtained by fitting the data in Table 2. These QSPRs are provided for both polymers and compound classes in the Supporting Information, Figure S11. It should

be stressed though, that the uncertainty accompanying the predicted $\log K_{\text{p-w}}$ values will depend on the chemical and the reliability of the $\log K_{\text{ow}}$ values used for the estimation.

Supporting Information—The Supporting Information includes tables with literature and new experimental $\log K_{\text{p-w}}$ data; tables presenting quality assessment of all data; and figures presenting literature $\log K_{\text{p-w}}$ data as a function of $\log K_{\text{ow}}$ and $\log K_{\text{p-w}}$ values determined in the present study. These data are available on the Wiley Online Library at <https://doi.org/10.1002/etc.5333>.

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Data Availability Statement—Most data and metadata are available in the Supporting Information. Data, associated metadata, and calculation tools are available from the corresponding author (m.t.o.jonker@uu.nl).

REFERENCES

- Adams, R. G., Lohmann, R., Fernandez, L. A., MacFarlane, J. K., & Gschwend, P. M. (2007). Polyethylene devices: Passive samplers for measuring dissolved hydrophobic organic compounds in aquatic environments. *Environmental Science & Technology*, 41, 1317–1323.
- Bao, L. J., Xu, S. P., Liang, Y., & Zeng, E. Y. (2012). Development of a low-density polyethylene-containing passive sampler for measuring dissolved hydrophobic organic compounds in open waters. *Environmental Toxicology and Chemistry*, 31, 1012–1018.
- Booij, K., Hofmans, H. E., Fischer, C. V., & Van Weerlee, E. M. (2003). Temperature-dependent uptake rates of nonpolar organic compounds by semipermeable membrane devices and low-density polyethylene membranes. *Environmental Science & Technology*, 37, 361–366.
- Booij, K., Robinson, C. D., Burgess, R. M., Mayer, P., Roberts, C. A., Ahrens, L., Allan, I. J., Brant, J., Jones, L., Kraus, U. R., Larsen, M. M., Lepom, P., Petersen, J., Pröfrock, D., Roose, P., Schäfer, S., Smedes, F., Tixier, C., Vorkamp, K., & Whitehouse, P. (2016). Passive sampling in regulatory chemical monitoring of nonpolar organic compounds in the aquatic environment. *Environmental Science & Technology*, 50, 3–17.
- Booij, K., Smedes, F., & Allan, I. J. (2017). Guidelines for determining polymer-water and polymer-polymer partition coefficients of organic compounds. *ICES Techniques in Marine Environmental Sciences*, 61, 32.
- Choi, Y., Cho, Y. M., & Luthy, R. G. (2013). Polyethylene-water partitioning coefficients for parent- and alkylated-polycyclic aromatic hydrocarbons and polychlorinated biphenyls. *Environmental Science & Technology*, 47, 6943–6950.
- DiFilippo, E. L., & Eganhouse, R. P. (2010). Assessment of PDMS-water partition coefficients: Implications for passive environmental sampling of hydrophobic organic compounds. *Environmental Science & Technology*, 44, 6917–6925.
- Eganhouse, R. P. (2016). Determination of polydimethylsiloxane-water partition coefficients for ten 1-chloro-4-[2,2,2-trichloro-1-(4-chlorophenyl)ethyl]benzene-related compounds and twelve polychlorinated biphenyls using gas chromatography/mass spectrometry. *Journal of Chromatography A*, 1438, 226–235.
- Endo, S., Hale, S. E., Goss, K. U., & Arp, H. P. H. (2011). Equilibrium partition coefficients of diverse polar and nonpolar organic compounds to

- polyoxymethylene (POM) passive sampling devices. *Environmental Science & Technology*, 45, 10124–10132.
- Fernandez, L. A., Harvey, C. F., & Gschwend, P. M. (2009). Using performance reference compounds in polyethylene passive samplers to deduce sediment porewater concentrations for numerous target chemicals. *Environmental Science & Technology*, 43, 8888–8894.
- Ghosh, U., Driscoll, S. K., Burgess, R. M., Jonker, M. T. O., Reible, D., Gobas, F., Choi, Y., Apitz, S. E., Maruya, K. A., Gala, W. R., Mortimer, M., & Beegan, C. (2014). Passive sampling methods for contaminated sediments: Practical guidance for selection, calibration, and implementation. *Integrated Environmental Assessment and Management*, 10, 210–223.
- Gilbert, S., Witt, G., Smedes, F., & Mayer, P. (2016). Polymers as reference partitioning phase: Polymer calibration for an analytically operational approach to quantify multimedia phase partitioning. *Analytical Chemistry*, 88, 5818–5826.
- Grant, S., Schacht, V. J., Escher, B. I., Hawker, D. W., & Gaus, C. (2016). Experimental solubility approach to determine PDMS-water partition constants and PDMS activity coefficients. *Environmental Science & Technology*, 50, 3047–3054.
- Hale, S. E., Martin, T. J., Goss, K. U., Arp, H. P. H., & Werner, D. (2010). Partitioning of organochlorine pesticides from water to polyethylene passive samplers. *Environmental Pollution*, 158, 2511–2517.
- Hsieh, M. K., Fu, C. T., & Wu, S. C. (2011). Simultaneous estimation of glass-water distribution and PDMS-water partition coefficients of hydrophobic organic compounds using simple batch method. *Environmental Science & Technology*, 45, 7785–7791.
- Jonker, M. T. O. (2016). Determining octanol–water partition coefficients for extremely hydrophobic chemicals by combining “slow stirring” and solid-phase microextraction. *Environmental Toxicology and Chemistry*, 35, 1371–1377.
- Jonker, M. T. O., Burgess, R. M., Ghosh, U., Gschwend, P. M., Hale, S. E., Lohmann, R., Lydy, M. J., Maruya, K. A., Reible, D., & Smedes, F. (2020). Ex situ determination of freely dissolved concentrations of hydrophobic organic chemicals in sediments and soils: Basis for interpreting toxicity and assessing bioavailability, risks and remediation necessity. *Nature Protocols*, 15, 1800–1828.
- Jonker, M. T. O., & Koelmans, A. A. (2002). Sorption of polycyclic aromatic hydrocarbons and polychlorinated biphenyls to soot and soot-like materials in the aqueous environment: Mechanistic considerations. *Environmental Science & Technology*, 36, 3725–3734.
- Jonker, M. T. O., & Muijs, B. (2010). Using solid phase micro extraction to determine salting-out (Setschenow) constants for hydrophobic organic chemicals. *Chemosphere*, 80, 223–227.
- Jonker, M. T. O., & van der Heijden, S. A. (2007). Bioconcentration factor hydrophobicity cutoff: An artificial phenomenon reconstructed. *Environmental Science & Technology*, 41, 7363–7369.
- Jonker, M. T. O., van der Heijden, S. A., Adelman, D., Apell, J. N., Burgess, R. M., Choi, Y., Fernandez, L. A., Flavetta, G. M., Ghosh, U., Gschwend, P. M., Hale, S. E., Jalalizadeh, M., Khairy, M., Lampi, M. A., Lao, W., Lohmann, R., Lydy, M. J., Maruya, K. A., Nutile, S. A., ... Wu, Y. (2018). Advancing the use of passive sampling in risk assessment and management of sediments contaminated with hydrophobic organic chemicals: Results of an international ex situ passive sampling interlaboratory comparison. *Environmental Science & Technology*, 52, 3574–3582.
- Jonker, M. T. O., van der Heijden, S. A., Kotte, M., & Smedes, F. (2015). Quantifying the effects of temperature and salinity on partitioning of hydrophobic organic chemicals to silicone rubber passive samplers. *Environmental Science & Technology*, 49, 6791–6799.
- Lee, H., Shim, W. J., & Kwon, J. H. (2014). Sorption capacity of plastic debris for hydrophobic organic chemicals. *Science of the Total Environment*, 470–471, 1545–1552.
- Lohmann, R. (2012). Critical review of low-density polyethylene's partitioning and diffusion coefficients for trace organic contaminants and implications for its use as a passive sampler. *Environmental Science & Technology*, 46, 606–618.
- Lohmann, R., Muir, D., Zeng, E. Y., Bao, L. J., Allan, I. J., Arinaitwe, K., Booi, K., Helm, P., Kaserzon, S., Mueller, J. F., Shibata, Y., Smedes, F., Tsapakis, M., Wong, C. S., & You, J. (2017). Aquatic global passive sampling (Aqua-Gaps) revisited: First steps toward a network of networks for monitoring organic contaminants in the aquatic environment. *Environmental Science & Technology*, 51, 1060–1067.
- Mayer, P., Vaes, W. H. J., & Hermens, J. L. M. (2000). Absorption of hydrophobic compounds into the poly(dimethylsiloxane) coating of solid-phase microextraction fibers: High partition coefficients and fluorescence microscopy images. *Analytical Chemistry*, 72, 459–464.
- Muijs, B., & Jonker, M. T. O. (2009). Temperature-dependent bioaccumulation of polycyclic aromatic hydrocarbons. *Environmental Science & Technology*, 43, 4517–4523.
- Paschke, A., & Popp, P. (2003). Solid-phase microextraction fibre-water distribution constants of more hydrophobic organic compounds and their correlations with octanol-water partition coefficients. *Journal of Chromatography A*, 999, 35–42.
- Perron, M. M., Burgess, R. M., Ho, K. T., Pelletier, M. C., Friedman, C. L., Cantwell, M. G., & Shine, J. P. (2009). Development and evaluation of reverse polyethylene samplers for marine phase II whole-sediment toxicity identification evaluations. *Environmental Toxicology and Chemistry*, 28, 749–758.
- Perron, M. M., Burgess, R. M., Suuberg, E. M., Cantwell, M. G., & Pennell, K. G. (2013). Performance of passive samplers for monitoring estuarine water column concentrations: 1. Contaminants of concern. *Environmental Toxicology and Chemistry*, 32, 2182–2189.
- Reitsma, P. J., Adelman, D., & Lohmann, R. (2013). Challenges of using polyethylene passive samplers to determine dissolved concentrations of parent and alkylated PAHs under cold and saline conditions. *Environmental Science & Technology*, 47, 10429–10437.
- Sabljić, A., Gusten, H., Hermens, J., & Opperhuizen, A. (1993). Modeling octanol/water partition coefficients by molecular topology: Chlorinated benzenes and biphenyls. *Environmental Science & Technology*, 27, 1394–1402.
- Smedes, F. (2019). SSP silicone–lipid– and SPMD–water partition coefficients of seventy hydrophobic organic contaminants and evaluation of the water concentration calculator for SPMD. *Chemosphere*, 223, 748–757.
- Smedes, F., Geertsma, R. W., Van der Zande, T., & Booi, K. (2009). Polymer-water partition coefficients of hydrophobic compounds for passive sampling: Application of cosolvent models for validation. *Environmental Science & Technology*, 43, 7047–7054.
- Ter Laak, T. L., Barendregt, A., & Hermens, J. L. M. (2006). Freely dissolved pore water concentrations and sorption coefficients of PAHs in spiked, aged, and field-contaminated soils. *Environmental Science & Technology*, 40, 2184–2190.
- Yang, Z. Y., Greenstein, D., Zeng, E. Y., & Maruya, K. A. (2007). Determination of poly(dimethyl)siloxane-water partition coefficients for selected hydrophobic organic chemicals using ¹⁴C-labeled analogs. *Journal of Chromatography A*, 1148, 23–30.
- Zeng, E. Y., Tsukada, D., Noblet, J. A., & Peng, J. (2005). Determination of polydimethylsiloxane-seawater distribution coefficients for polychlorinated biphenyls and chlorinated pesticides by solid-phase microextraction and gas chromatography-mass spectrometry. *Journal of Chromatography A*, 1066, 165–175.
- Zhu, T., Jafvert, C. T., Fu, D., & Hu, Y. (2015). A novel method for measuring polymer-water partition coefficients. *Chemosphere*, 138, 973–979.