# Silicone–water partition coefficients determined by cosolvent method for chlorinated pesticides, musks, organo phosphates, phthalates and more

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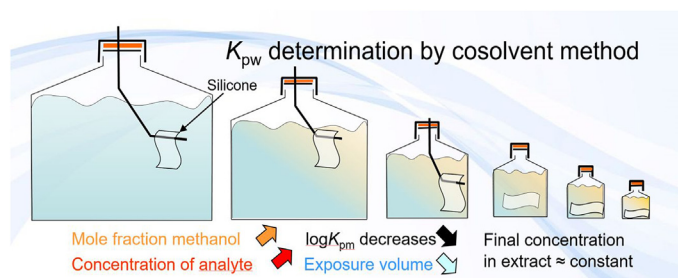[b] Deltares, PO. Box 85467, 3508 AL, Utrecht, the Netherlands

## HIGHLIGHTS

- Eighty silicone–water partition co-efficients of hydrophobics for passive sampling.
- The cosolvent method provides partition coefficients with adequate quality assessment.
- Hydrophobicity and structure determine silicone–water partition coefficients.

## GRAPHICAL ABSTRACT

## ABSTRACTS

To further support implementation of monitoring by passive sampling, robust sampler–water partition coefficients ($K_{pw}$) are required to convert data from passive sampler into aqueous phase concentrations. In this work silicone–water partition coefficients were determined for ~80 hydrophobic organic contaminants using the cosolvent method. Partition coefficients ($K_{pm}$) were measured in pure water and water-methanol mixtures up to a methanol mole fraction of 0.3 (50% v/v). Subsequently, $\log K_{pw}$ in pure water was determined as the intercept of linear regression of the $\log K_{pm}$ with the corresponding methanol mole fractions. $\log K_{pw}$ were determined for phthalates, musks, organo phosphorus flame-retardants, chloro-benzenes, pesticides, some PCBs and a number of miscellaneous compounds. The median standard error and 95% confidence interval of the measured $\log K_{pw}$ was 0.06 and 0.13, respectively. The overall relationship between $K_{pw}$ and $K_{ow}$ seems insufficient to predict $K_{pw}$ for unknown compounds. Prediction may work within a group of compounds with similar nature, e.g. homologues but HCH isomers having the same $K_{ow}$ exhibit $K_{pw}$ ranging over an order of magnitude. Long alkyl-chain phthalates and tris(2-ethylhexyl) phosphate; all having a molecular volume >400 Å$^3$, deviated the most from the $K_{pw}$–$K_{ow}$ relationship.

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## 1. Introduction

Passive sampling is increasingly used to assess environmental quality with regard to concentrations of pollutants in the aqueous environment, including water, sediment and biota tissue. With passive sampling the freely dissolved concentration ($C_w$) of neutral hydrophobic organic compounds (HOC) is determined while

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legislation for HOC is based on total concentrations, what is already under debate for a long time (Smedes, 1994). The $C_w$ is proportional to the chemical activity and therefore represents the driving force for transport to other media, like uptake by organisms (Ditoro et al., 1991; Reichenberg and Mayer, 2006). Passive sampling is suggest as a "chemometer" for comparison of HOC levels over multiple media in the environment (Jahnke et al., 2014). For passive sampling of the water phase semi-permeable membrane devices (SPMD), i.e. low−density polyethylene lay−flat tubing filled with triolein (Huckins et al., 2006), were historically frequently used for monitoring of HOC. Nowadays single−phase samplers constructed from LDPE (Adams et al., 2007), silicone (Smedes, 2007), or polyoxymethylene (Cornelissen et al., 2008), are more commonly applied. For simpler modelling of the water−sampler exchange, it is important that HOC's internal diffusion in the polymer is sufficiently high and only the transport resistance in water boundary (WBL) layer controls the sampler uptake (Rusina et al., 2007)., HOC's polymer diffusion coefficients are, however, too low for polyoxymethylene to attain WBL controlled uptake conditions, are mostly high enough for LDPE, and very high for silicones, making the latter a very suitable material for construction of passive samplers. Under fully WBL controlled uptake, the sampler exchange rate can be determined from the release of performance reference compounds (PRC), dosed to the sampler prior to exposure (Booij et al., 1998; Booij and Smedes, 2010; Rusina et al., 2010). To convert measured HOC uptake in exposed passive samplers into aqueous phase concentrations, sampler−water partition coefficients ($K_{pw}$) are required for target HOC, as well as for PRC. In literature $K_{pw}$ are available for polycyclic aromatic hydrocarbons (PAH), polychlorobiphenyls (PCB), including a suite of PCB absent in industrial mixtures that can be utilized as PRC (Smedes et al., 2009). Furthermore, $K_{pw}$ are published for musks, organo phosphates and UV filters (Pintado-Herrera et al., 2016). Accurate measurement of $K_{pw}$ values can be hampered by presence of a "third phase", i.e. particulates and/or dissolved organic material, sorbing HOC and enhancing the water concentration. Co-extraction of the HOC adsorbed to those particulates together with the water dissolved fraction easily leads to an over estimation of the freely dissolved aqueous concentration. Low concentrations of HOC in water are further easily affected due to sorption on container walls, stirrers, particulate matter etc. Smedes et al. (2009) validated $K_{pw}$ measurement for pure water extrapolating partition coefficients measured in water-methanol mixtures ($K_{pm}$) to only water. With increasing methanol content, $K_{pm}$ decreases, as well as a possible particulate bound fraction (third phase), while on the other hand the aqueous concentration increases, making accurate $K_{pm}$ measurement possible. For PCB and PAH, the log$K_{pm}$ showed a linear relationship with the methanol mole fraction (Mf) (Smedes et al., 2009):

$$\log K_{pm} = \log K_{pw} - \sigma Mf \tag{1}$$

where $\sigma$ is the slope between log$K_{pm}$ and Mf. The present paper reports on the application of the cosolvent approach for the determination of $K_{pw}$ for phthalates, musks, organo phosphorus flame retardants (OPFR), chlorobenzenes, chlorinated pesticides, a number of miscellaneous HOC, and some PCB that can be potentially used as PRC. Additionally, $K_{pw}$ measurements were repeated for PCB already established as PRC.

## 2. Material and methods

### 2.1. Materials

Solvents used include ethyl acetate, methanol, acetonitrile, acetone and hexane that were of analytical grade and were used without further purification. Translucent Altesil™ silicone rubber sheets (0.5 mm thick) were obtained from www.alteceweb.com (UK). The polymer sheets were cut into pieces of 5.5 × 9.5 cm weighing approximately 3.3 g (two-sided surface area is 100 cm2). Prior to use, sheets were soxhlet extracted with ethyl acetate for one week to remove low oligomers. One spike mixture of all HOC standards obtained from various suppliers was prepared, A list of compounds is given in Supplementary Information S1 together with their CAS No., and properties: MW, $K_{ow}$ and molecular volume obtained from Molinspiration (2017). Equilibration of the silicone sheets with aqueous solutions was performed in Duran bottles of 0.5−10 L.

### 2.2. Silicone rubber spiking

The silicone rubber sheets were spiked with HOC using methanol−water mixtures (Booij et al., 2002). Fourteen silicone rubber sheets were transferred to a 1 L jar, followed by addition of 150 mL methanol, 30 mL Milli-Q water and the HOC spike mixture, where after the jar was shaken for 48 h. Then 30, 40, and 50 mL of Milli-Q water and was added stepwise continuing the shaking for 48, 120 and 240 h respectively. After 240 h the solvent was drained, and the sheets washed briefly with 200 mL Milli-Q water and shaken overnight in 100 mL Milli-Q water. The HOC approximate amounts spiked per sheet are listed in Supplementary information S1.

### 2.3. Equilibrations

Water and methanol were mixed by weight to obtain the methanol/water mole fractions (Mf) as listed in Table 1. For equilibrations with pure water, 10 L bottles were used, while gradually smaller bottles were used as the methanol content increased. The bottles were rinsed with acetone and Milli-Q water before use. A stainless steel rod was mounted through the top in all bottles larger than 1 L to position the sheet as a flag close to the bottle wall (Fig. 1) where flow is highest during orbital shaking. In equilibrations with pure water analyte concentrations are very low, but steadily increase by several orders of magnitude towards the highest methanol fraction (Mf = 0.3). The setup with decreasing volumes ensures a small concentration range in the final water extracts, supporting more precise instrumental analysis. In equilibration 1 a non-spiked sheet was exposed to water spiked with a HOC mixture. In the other equilibrations the HOC spiked sheets were exposed as described above. For the equilibrations amber bottles were used, or when not available, the bottles were protected from light by wrapping in aluminum foil. Bottles were shaken on a Gerhardt orbital shaker with an amplitude of 3 cm at 100 rpm for three months. After equilibration, the sheets were retrieved from the solution, carefully wiped dry with a paper tissue and stored at −20 °C in an amber jar with an aluminum foil lined lid.

### 2.4. Extraction of the aqueous phase

The large volume equilibrations with pure water and 9%

**Table 1**
Overview of performed equilibrations.

| Eq. No. | Volume L | Mf methanol | Percentage % w/w | Way of spiking |
|---|---|---|---|---|
| 1 | 9.8 | 0 | 0 | Aqueous spike |
| 2 | 9.2 | 0 | 0 | Sheet spike[a] |
| 3 | 9.4 | 0 | 0 | Sheet spike |
| 4 | 8.1 | 0.050 | 9 | Sheet spike |
| 5 | 3.5 | 0.102 | 17 | Sheet spike |
| 6 | 1.9 | 0.150 | 24 | Sheet spike |
| 7 | 0.8 | 0.191 | 30 | Sheet spike |
| 8 | 0.35 | 0.250 | 37 | Sheet spike |
| 9 | 0.27 | 0.299 | 43 | Sheet spike |
| 10 | 0.36 | 0.247 | 37 | Sheet spike |

[a] Weight of a sheet was approximately 3.3 g.