Development and validation of a new method to upload polymers with super-hydrophobic contaminants for passive dosing approaches

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Introduction

Contaminant uploaded polymers are increasingly used as delivery mechanisms for analytes into experimental systems (passive dosing). The concept of passive dosing was initially developed for the purpose of toxicity testing, where it allowed the delivery of a defined and constant dose to test organisms[1, 2]. The advantages have also been recognised for other applications, such as the determination of equilibrium sorption and speciation of hydrophobic contaminants in systems involving water, dissolved and solid hydrophobic phases[3-6], as well as an alternative spiking approach for poorly soluble contaminants to aqueous test systems[5]. Passive dosing approaches, however, rely on precise and reproducible methods to load contaminants to the polymer. This is particularly important when working with superhydrophobic contaminants (SHOCs; log K_{OW} >7) since measuring water phase concentrations is rarely feasible for such compounds, and aqueous concentrations are thus typically calculated under mass balance assumptions using measured concentrations in the polymer at equilibrium and known polymer-water partition coefficients.

To date, contaminants are typically loaded to passive dosing polymers via direct partitioning from methanol or a methanol-water mix. While this partitioning driven upload method has been performed with highly reproducibility for a wide range of contaminants, variability in the mass loaded has been reported to increase with increasing contaminant hydrophobicity. For example Endo et al. (2013)[10] reported increasing variability of PBDEs loaded to poly(dimethylsiloxane) (PDMS), with up to 40% (relative standard deviation (RSD)) for BDE 209 (log K_{OW} >9). A pilot study performed in our laboratory demonstrated similar variability for a range of PCDDs (log K_{OW} 6.9-8.3) loaded to PDMS, with up to 47% RSD for the most hydrophobic, OCDD. The high variability in the loaded masses contribute undesirably high uncertainties to the experimental data. In addition, slow partitioning kinetics result in inconvenient waiting times before the polymers are ready for deployment in the experimental system. Here we present a new polymer loading approach that overcomes these limitations, and achieves precise, rapid and reproducible SHOC concentrations in PDMS to provide a robust basis for passive dosing approaches.

Theory

Solvents like toluene and hexane have been reported to swell PDMS by a factor of 1.3 in any one dimension (which equates to an increase in volume of 2.2)[7]. During the swelling process, analytes dissolved in the solvent are transported into the PDMS where they remain after the solvent is evaporated[2]. Swelling can therefore significantly increase the mass of analyte loaded in a polymer compared to partitioning alone. A simplified model of the combined swelling and partitioning loading process predicts that the majority of SHOC mass in PDMS is achieved via swelling (e.g. range 82-90% of total mass for five PCDDs with log K_{OW} ranging from 6.9 to 8.3). The swelling method has several potential advantages, including 1) loading can be achieved rapidly since the process does not rely on partitioning kinetics which are typically very slow for SHOCs, and 2) the mass of analyte loaded is largely independent of its physico-chemical properties, being primarily driven by the concentration in the loading solvent, and the mass can thereby be easily controlled. Therefore, loading extremely hydrophobic organic contaminants (extreme SHOCs, e.g. OCDD, PCB 209) via swelling into PDMS may be a faster and more reliable loading method.

Two potential issues were identified that could arise when loading passive dosing polymers via the swelling approach, and were investigated in this study:

1. Potential trapping of analytes: SHOCs, and in particular extreme SHOCs, are often large molecules which, when loaded via swelling, may potentially be trapped in the PDMS after the solvent has evaporated (de-swelling). Consequently, large molecules such as OCDD might not be available for subsequent dosing and partitioning processes.

2. Exceeding solubility: The maximum solubility of SHOCs in the PDMS may be exceeded when loading via the swelling approach. For some applications of passive dosing it is essential to stay below saturation limits in the PDMS to ensure that equilibrium concentrations in the dosing polymer and a depletion phase are below maximum solubility, or to, for example, avoid mixtures effects close to solubility. Therefore, it is important to know the maximum solubility of SHOCs in PDMS.

Material and Methods

Materials: Coated fibres were obtained from Fibreguide Industries Inc (Stirling, USA) and consisted of a 50 µm layer of PDMS coated on a glass fibre of diameter 100 µm. PDMS sheeting, thickness 7.5 µm, was obtained from Specialty Silicone Products, Inc (New York, USA). A PCDD mix of 2,3,7,8-TCDD, 1,2,3,7,8-PeCDD, 1,2,3,4,7,8-HxCDD, 1,2,3,4,6,7,8-HpCDD and OCDD was purchased from AccuStandard (New Haven, USA), and 1,2,3,4,6,7,8-HpCDF (used as an internal standard) from Cambridge Isotopes Laboratory (Andover, USA). Standard solutions for PCBs 136, 182, 204, 206 and 209 as well as solid PCB 209 and PCB 118 (used as internal standard) were obtained from AccuStandard (New Haven, USA). All solvents used were of analytical grade.

Swelling load method: The swelling load method was tested for consistency and reliability using a mixture of the five PCDD congeners (in toluene) and five PCBs (in isooctane) listed above, which differ in their physico-chemical properties. To perform the experiment, PDMS coated fibres were cut into 2 cm pieces, washed in MilliQ water and dried for 24 h. PDMS fibres were then transferred into a 20 mL vial and swelled in hexane for 24 h to clean and remove unpolymerised PDMS oligomers[7]. After all solvent was evaporated, PDMS fibres were weighed using a Mettler microbalance and subsequently stored in methanol. The variability (relative standard deviation, %RSD) in PDMS weight between fibres was less than 2%.
For the swelling load, PDMS fibres were transferred to 2 mL vials containing 1.8 mL of 0.7 µg mL^{-1} PCDD standard in toluene, or 1.8 mL of 3.5 µg mL^{-1} PCB standard in isoctane. The PCDD/PCB concentrations in the loading solvent were calculated (based on known swelling ratios for the loading solvent) to ensure that the loaded concentration in the PDMS after swelling was below maximum solubility of the most hydrophobic congener (see method below to determine maximum solubilities). To ensure an even swelling, fibres were completely submerged in the loading solution. The loading vial was placed onto an orbital shaker in an incubator (23°C, 100 rpm) for 24 h. Loaded PDMS fibres were transferred onto dry lint-free tissue and immediately separated. To establish the concentration in the PDMS after loading and quantify the variability between fibres, individual PDMS fibres were transferred to inserts and extracted in 270 µL of hexane for 24 h on an orbital shaker (23°C, 100 rpm). Based on previous tests, one extraction step was found to be exhaustive (>99% of mass recovered). The hexane extracts were evaporated under a N_2 stream to just dryness. 20 µL of the injection standard 1,2,3,4,6,7,8-HpCDF or PCB 118 of known concentration was added for PCDDs and PCBs, respectively. Extracts were analysed as described below.

Potential trapping of analytes: To ensure free availability of the total mass of analytes loaded, swelling loaded PDMS fibres were depleted using a swelling and a non-swelling solvent. If analytes are trapped in the polymer post-loading, the non-swelling solvent would be expected to recover less mass than the swelling solvent. To test for potential trapping of analytes, 2 cm PDMS fibres (n=20) were loaded in 2.5 µg mL^{-1} PCDD standard mix using the swelling load (as described above) and two fibres each were subsequently transferred into 2 mL glass vials. Two mL of a non-swelling solvent (methanol) was added and each of the 5 fibre pairs was depleted for 24 h on an orbital shaker (23 °C, 100 rpm). Each fibre pair was extracted a further four times. The extracts were combined and analysed as described for the swelling load. The remaining 5 PDMS fibre pairs were extracted in a swelling solvent (hexane) using the same method as for methanol except only one extract was required.

Maximum solubilities in PDMS: To date, no data on maximum solubilities of SHOCs in PDMS are available. The maximum solubility of analytes can, however, be measured via PDMS-PDMS partitioning of analytes from super-saturated PDMS sheets loaded via swelling (at concentrations orders of magnitude higher than the expected PDMS solubility) into clean PDMS fibres. The equilibrium concentration in the clean fibres provides the solubility limit in PDMS. To determine the maximum solubility in PDMS for the least soluble tested SHOCs (HpCDD, OCDD, PCB 209) PDMS sheets of dimensions 2.5 x 1.5 x 0.0075 cm were prepared as previously described for fibres. Two PDMS sheets were submerged for 24 h in 2 mL of 15 µg mL^{-1} PCDD standard mix in toluene. Predicted concentrations of each congener in the PDMS sheets were in excess of 25 ng μL^{-1}. A further

two PDMS sheets were submerged for 48 h in 2.2 mL of 940 µg mL^{-1} PCB 209-solution, premade from solid PCB 209 in toluene. Predicted concentration of PCB 209 in the PDMS sheets was approximately 1,460 ng $µL^{-1}$. After loading, the PDMS sheets were placed on Teflon sheeting to allow the toluene to completely evaporate. Two cm clean PDMS fibres were tightly sandwiched between either the two PCDD loaded, or the two PCB 209 loaded sheets. Maximum contact between loaded sheets and the fibres was ensured by weighing the top sheets down. Replicate PDMS fibres (5 replicates PCDDs, 3 replicates PCB 209) were taken out after different times (to establish when equilibrium was reached), wiped with a lint free tissue to remove surface adsorbed analyte, and extracted in 270 µL hexane for 24 h on an orbital shaker (23°C, 100 rpm). Based on previous tests, one extraction step was found to be exhaustive for PCDDs (>99% of mass recovered). A second 24 h extraction for PCB 209 was performed and the two extracts combined for analysis.

Instrumental analysis: The concentration of PCDDs and PCBs in the PDMS fibre extracts were quantified on a Hewlett Packard 5890 Gas Chromatography-Electron Capture Detector (GC-ECD) Series II with a DB-5 fused silica capillary column (30 m × 0.25 mm i.d.) (Agilent Technologies, Santa Clara, USA).
PCDD concentrations were quantified based on their peak area relative to the internal standard 1,2,3,4,7,8,9-HpCDF, and using a 5-point calibration series consistent of 50-800 pg $µL^{-1}$ PCDD mix and containing 300 pg $µL^{-1}$ 1,2,3,4,7,8,9-HpCDF. The PCB concentrations were quantified with PCB 118 as internal standard and the concentration for the calibration series was 100-1,600 pg $µl^{-1}$, containing 200 pg $µL^{-1}$ PCB 118.

Results and discussion:
Using a PCDD loading concentration of 0.7 µg mL^{-1} in 1.8 mL toluene (1.26 µg mass) the loaded PDMS contained approximately 1.5 µg mL^{-1} (range 1.3-1.6 µg mL^{-1}, or 1.16 ng mass) of each congener after swelling (Figure 1). For the PCBs, a higher loading concentration of 3.5 µg mL^{-1} per congener (6.3 µg mass) in isooctane resulted in loaded PDMS concentration of approximately 8.9 µg mL^{-1} (range 8.7–9.2 µg mL^{-1}, 6.95 ng mass, Figure 1). The consistent PDMS concentrations for all five PCDDs (log K_{OW} = 6.9-8.3)[8], and the five PCBs (log K_{OW} = 6.22-8.2)[9] indicate that loading via swelling is mostly independent of the analyte's physico-chemical properties. By contrast, the methanol and methanol-water partitioning loading methods result in increasing loaded mass with increasing compound hydrophobicity[10].

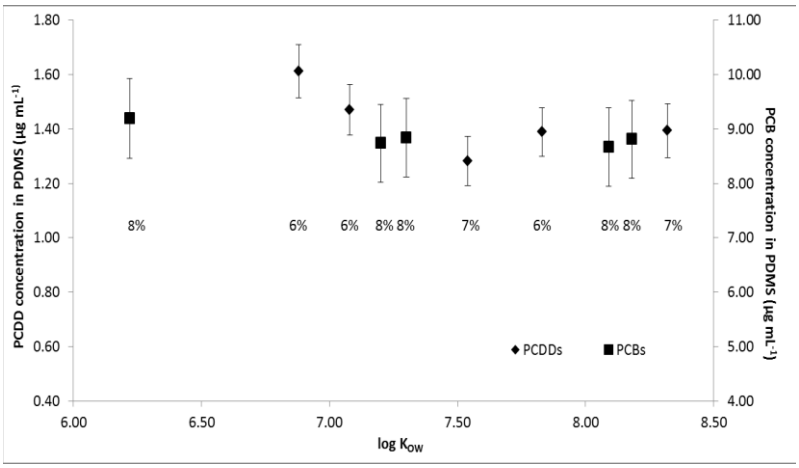

Figure 1. Concentrations of PCDDs (left axis scale) and PCBs (right axis scale) in the PDMS fibre using the swelling load method with toluene and isooctane, respectively. Error bars represent the standard deviation. Values of the relative standard deviation % (RSD) are given for each

The swelling method resulted in low variability of PCDD concentrations between PDMS fibres for all congeners (%RSD = 6.0–7.1% n = 5 (Figure 1)), indicating high reproducibility of the loading method. Similarly, highly reproducible results were observed for PCB concentrations in PDMS loaded using isooctane which has a similar swelling ratio to toluene (%RSD = 8.0–8.3% n = 5 (Figure1)). Furthermore the variability was not observed to increase with increasing hydrophobicity of the congeners as was found for the methanol partitioning loading method for SHOCs[10].

In comparison to partitioning based loading methods which require several days to achieve equilibrium (e.g. up to 7 days)[10], a major advantage of the swelling method is that equilibrium is not required and highly reproducible loading can be completed within 24 hours (and possibly even less time since the swelling process was observed to be very rapid). A further advantage of the swelling method is that the mass of SHOCs loaded into the polymer is primarily driven by swelling and therefore the expected mass loaded from any solvent can be readily predicted based on the swelling

ratio for the loading solvent. A comprehensive list of solvent swelling ratios for PDMS has been reported by Lee et al. (2003)[7].

The practical application of swelling-loaded polymers for passive dosing studies requires, however, that large molecules are not trapped in the polymer following de-swelling and that maximum solubilities in PDMS are not exceeded after loading. To investigate whether large compounds are trapped in the polymer after de-swelling, the recoveries of OCDD, as one of the largest model SHOCs used, were compared via extraction in a swelling and a non-swelling solvent. Almost identical masses of OCDD were depleted from the swelling loaded PDMS fibres (loaded concentration exceeded OCDD solubility) using a swelling solvent (hexane: extracted mass average 3.4 ng, n=5, %RSD 6.2%), and a non-swelling solvent (methanol: extracted mass average 3.6 ng, n=5, %RSD 8.2%). The OCDD trap-test validated the use of swelling as a feasible loading method as high molecular weight SHOCs loaded to the passive dosing polymer are freely available for partitioning depletion and passive dosing.

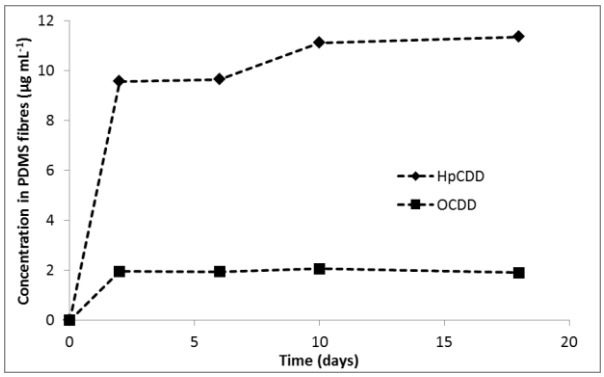

Figure 2. HpCDD and OCDD partitioning into clean PDMS fibres via PSMS-PSMS partitioning over time. Maximum solubility occurred after approximately 10 days for HpCDD and 2 days for OCDD.

The maximum solubilities of HpCDD and OCDD in PDMS were determined to be 11 and 1.9 µg mL^{-1}, respectively. Due to the lower mass transfer of OCDD from the loaded PDMS sheets into the clean PDMS fibre (1.49 ng compared to 8.91 ng of HpCDD in the clean PDMS at equilibrium), equilibrium was reached within 2 days compared to approximately 10 days for HpCDD (Figure 2). By comparison to the PCDDs, the maximum solubility of PCB 209 was significantly higher at 530 µg mL^{-1} (equilibrium was achieved within 40 days). The high value was surprising as the three compounds have similar hydrophobicities (log K_{OW} for HpCDD, OCDD and PCB 209 of 7.8, 8.3 and 8.2, respectively) and similar water solubilities (S_W of approximately 9.4, 1.2 and 6.2 ng L^{-1}, respectively), indicating similar saturation concentrations in octanol. The difference in molecular configuration between the two planar PCDD congeners and PCB 209 (which occupies a larger 3 dimensional space) may confer differences in physico-chemical properties that explain the higher activity of PCB 209 in PDMS.

Knowing the maximum solubilities in PDMS for the least soluble SHOCs means that, for the swelling load, the concentration in the loading solution can be selected to achieve very specific concentrations in the loaded polymer. As a consequence, experimental set-ups can be accurately adjusted to meet criteria regarding the maximum solubility as well as instrument detection limits.

The results from these experiments suggest that the swelling load method represents a simple, rapid and robust approach to achieve accurate and reproducible loaded masses of SHOCs with log K_{OW} up to 8.3 in polymers for passive dosing and other applications. The method has been shown to work with two loading solvents that have similar swelling ratios for PDMS, toluene and isooctane, and for two compound groups. Future work will focus on understanding the differences in maximum solubilities of PCDDs and PCBs in PDMS.

References:

1. Mayer P, Wernsing J, Tolls J, de Maagd PG-J, Sijm DTHM. (1999); *Environ Sci Technol*. 33(13): 2284-90.
2. Brown RS, Akhtar P, Åkerman J, Hampel L, Kozin IS, Villerius LA, et al. (2001); *Environ Sci Technol*. 35(20): 4097-102.
3. Grant S, Mortimer M, Stevenson G, Malcolm D, Gaus C. (2011); *Environmental Science & Technology*. 45(2): 406-11.
4. Birch H, Gouliarmou V, Holten Lützhøft H-C, Mikkelsen PS, Mayer P. (2010); *Anal Chem*. 82(3): 1142-6.
5. ter Laak TL, Durjava M, Struijs J, Hermens JLM. (2005); *Environ Sci Technol*. 39(10): 3736-42.
6. Kim S-J, Kwon J-H. (2010); *CLEAN – Soil, Air, Water*. 38(9): 797-802.
7. Lee JN, Park C, Whitesides GM. (2003); *Anal Chem*. 75(23): 6544-54.
8. Åberg A, MacLeod M, Wiberg K. (2008); *Journal of Physical and Chemical Reference Data*. 37(4): 1997-2008.
9. Hawker DW, Connell DW. (1988); *Environ Sci Technol*. 22(4): 382-7.
10. Endo S, Mewburn B, Escher BI. (2013); *Chemosphere*. 90(2): 505-11.