SURFACTANT FACILITATED TRANSPORT OF SUPER-HYDROPHOBIC CONTAMINANTS: POLYMER BASED METHODS TO INVESTIGATE PARTITIONING TO MICELLES

Sharon Grant[1]*, Veronika Schacht[1], C. Alexander Villa[1], Beate Escher[1] and Caroline Gaus[1]
[1] The University of Queensland, Entox, 39 Kessels Road, Coopers Plains, QLD, Australia

Introduction

The transport potential for chemicals in deposition matrices such as soil and sediments is strongly dependent on their water solubility and affinity for soil organic matter. Consequently, super-hydrophobic organic contaminants (SHOCs) which have low water solubility (C_W^{sat}) and high soil-water partitioning coefficients (K_d) are generally considered to be retained in the surface 5-10 cm of soils. Partitioning of SHOCs to surfactant micelles in soil-water, however, has been shown to significantly increase SHOC mobility in field soils[1]. This may lead to unexpected groundwater contamination and associated offsite transfer, posing risks for environmental and human exposure to toxic compounds. To predict surfactant facilitated transport (SFT) of SHOCs and thereby assess potential exposure risks, partitioning behavior between soil, water and surfactant phases must be understood and quantified. Experimental determination of partition coefficients is, however, challenging for extremely hydrophobic compounds (e.g. slow time to equilibrium, low aqueous concentrations, losses to glassware, difficulties with spiking poorly soluble compounds into water). Additionally, since surfactants are dissolved, classical separation based approaches to determine surfactant-water partitioning parameters cannot be used.

To address these experimental challenges, this study aimed to adapt and validate a novel approach to determine SHOC partition coefficients to surfactant micelles (K_{MI}), by measuring depletion of SHOC-loaded polymers by surfactant solutions[2,3]. This approach was developed to determine dissolved organic carbon-water partition coefficients[3] and has not been previously applied to measure partitioning to surfactants for SHOCs with octanol-water partitioning coefficients (K_{OW}) >$10^{6.9}$. For the present study, a model surfactant, sodium dodecyl sulfate (SDS), and five polychlorinated dibenzo-*p*-dioxins (PCDDs) covering a range of hydrophobicities (K_{OW} of $10^{6.9}$–$10^{8.3}$) were used. Poly(dimethylsiloxane) (PDMS) was selected for this study as preliminary experiments confirmed SDS partitioning into this polymer is negligible.

Theory

Surfactants are amphiphilic with a hydrophilic 'head' and a hydrophobic 'tail'. At the critical micelle concentration (CMC), surfactants aggregate into micelles which can readily transport with the aqueous phase via their hydrophilic surface layers, while non-polar contaminants can partition into their hydrophobic cores. Below CMC, surfactants exist solely as monomers in the aqueous phase and, for very hydrophobic compounds, facilitated transport with monomers may also occur[4]. At CMC, the aqueous concentration of monomers is maximised and any further surfactant added to the system is incorporated into micelles.

To determine the partitioning of SHOCs to surfactant micelles, SHOCs were uploaded into a known volume of PDMS and then added to a surfactant solution at a given concentration (above CMC) and left until equilibrium was reached. The mass of SHOCs depleted from the PDMS (which equals the mass in the aqueous, monomeric and micellar phases at equilibrium) was measured. Based on experimentally determined PDMS-water and monomer-water partitioning coefficients, the micelle-water partitioning coefficient, K_{MI}, was calculated from equation (1) below:

$$K_{MI} = \frac{1}{Mass_{Surf,MI}} \left(\frac{Mass_{SHOC,PDMS\ t=0}}{Mass_{SHOC,PDMS}} . V_{PDMS} . K_{PDMS-W} - V_{PDMS} . K_{PDMS-W} - K_{MO} . CMC . V_W - V_W \right) \quad (1)$$

where $Mass_{Surf,MI}$ is the mass of surfactant in micelles (mg) (calculated from the concentration of surfactant added less the monomer concentration which is equal to CMC when micelles are present), $Mass_{SHOC,PDMS\ t=0}$ is the mass of SHOCs loaded in the PDMS at time zero (ng), $Mass_{SHOC,PDMS}$ is the mass of SHOCs remaining in the PDMS at equilibrium (ng), V_{PDMS} is the volume of PDMS (ml), K_{PDMS-W} is the partitioning coefficient for the SHOC between PDMS and water (-), K_{MO} is the monomer-water partitioning coefficient (ml/mg), CMC is the critical micelle concentration (mg/ml) and V_W is the volume of water (ml).

Materials 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. Fibres were cut into 2 cm lengths (equivalent PDMS volume of 0.79 μl), weighed, cleaned for 24 hours in *n*-hexane and stored in methanol until use. 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 octa-CDD 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). SDS (purity ≥99%) was obtained from Sigma-Aldrich (Sydney, Australia). Manufacturer listed CMC for SDS was reported as 7-10 mM (average 8.5 mmol/L or 2,451 mg/L). Pure deionised water was prepared using a Millipore water purification system (Merck Millipore, Kilsyth, Australia). All solvents used were of analytical grade.

PCDD upload to PDMS. Initial experiments to upload the PCDD mix to PDMS discs (diameter 2 mm) were performed (cleaned, weighed discs were added to a spiked methanol upload solution for up to 120 hours until equilibrium was reached). However, increasing variability in uploaded masses with increasing PCDD congener hydrophobicity was observed (coefficient of variation (CV) for OCDD up to 47%). In subsequent experiments, PCDDs were uploaded to PDMS-coated glass fibres from a toluene-PCDD spiking solution. Fibres were immersed in 175 μl of toluene containing five PCDD congeners (each at 5 μg/ml), left on a shaker at 100 rpm for 24 hours, and then removed and air dried to evaporate remaining toluene. Toluene swells PDMS and the uploaded mass resulted from both partitioning (estimated at 10 and 18% for OCDD and TCDD, respectively) and swelling with PCDD-loaded toluene (82-90%). Replicate variability was reduced to less than 5.8% CV for all congeners. Fibres have the added benefit of higher surface area which increases partitioning kinetics. In addition, by increasing the uploaded mass of individual PCDD congeners through swelling, the volumes of PDMS and surfactant solution could be minimised whilst still remaining within analyte detection limits. Losses of SHOCs to glassware were therefore minimised.

Determination of partition coefficients using PDMS fibres. Loaded fibres were added to 50 μl glass inserts in 2 ml injection vials and 270 μl of SDS solution added at a concentration equal to three times CMC (7.35 mg/ml). The volume of PDMS and surfactant solution were optimised to predict ~50% depletion of the fibre. Ten loaded fibres were extracted immediately in 270 μl of *n*-hexane to determine the PCDD mass in the fibres at t=0. Initial experiments indicated that >98% of PCDDs were extracted from the fibres with a single extraction. Fibres were depleted in triplicate at a temperature of 25°C (in the dark) and removed from the SDS solution after 1, 3, 5, 7, 10 and 14 days. Fibres were cleaned in deionised water to remove surface sorbed SDS and then extracted in 270 μl *n*-hexane. Extracts were blown to near dryness and 15-20 μl toluene was added containing 300 pg/μL HpCDF as an internal standard.

Instrumental analysis: PCDD concentrations in the PDMS extraction were measured using a Hewlett Packard 5890 Series II gas chromatograph with an electron capture detector (GC-ECD) (Hewlett Packard, Ratingen, Germany) on a DB-5 fused silica capillary column (30 m × i.d. 0.25 mm). An external standard calibration dilution series (50-800 pg/μl) of the PCDD mix with 300 pg/μL HpCDF internal standard was used for peak quantification

Results and discussion

The high surface area of the PDMS-coated fibres resulted in relatively rapid equilibration kinetics, with the lower chlorinated, more water soluble PCDDs reaching equilibrium the quickest; i.e. TCDD (log K_{OW} 6.9)

within 2 days and OCDD (log K_{OW} 8.3) within 4 days. These equilibration times were significantly faster than predicted for PCDD partitioning from PDMS to water alone for the PDMS/water volume ratio used in this study (estimated at approximately 20 to 24 days for TCDD and OCDD, respectively, following the approach of Kwon et al[5]). This is consistent with reported passive dosing studies in the presence of other (non-micellar) colloids[6,7] and, in addition to the high fibre surface area, is attributable to the facilitation of PCDDs across the aqueous boundary layer by the surfactants present in the aqueous phase.

Calculated log K_{MI} values ranged from 5.7 to 6.2 for TCDD to OCDD (K_{MI} calculated on L/kg basis), with K_{MI} increasing with PCDD hydrophobicity (increasing K_{OW}) (Figure 1A). Replicate variability ranged from 0.07 to 0.11 log units within congeners, with the more hydrophobic congeners having the greatest variability. SDS-water partition coefficients have not been reported previously for PCDDs; however, K_{MI} values were consistently lower than those reported for polychlorinated biphenyls (PCBs) of similar hydrophobicity (Figure 1A). The calculation method for the micelle-water partition coefficients used in this study (equation 1) relies on data for K_{MO} (monomer-water partition coefficient) and K_{PDMS-W} (PDMS-water partition coefficient). The calculated K_{MI} value is relatively invariant to changes in K_{MO}, but is highly dependent on the values for K_{PDMS-W}. As can be seen from Figure 1B, reported values for K_{PDMS-W} are generally lower for PCDDs compared to other halogenated aromatic hydrocarbons (PCBs and PBDEs) with similar log K_{OW} values. This may contribute to the lower calculated values of K_{MI} for PCDDs compared to PCBs; for instance, recalculating K_{MI} using equation 1 and the data from the present study but substituting K_{PDMS-W} values reported for PCBs, generates K_{MI} values comparable to those reported for PCBs in the literature. Only recently have novel approaches to determine K_{PDMS-W} values for super-hydrophobic compounds emerged in the literature[5], and as more data becomes available the reported variability in these values for PCDDs, and the concomitant effect on determined K_{MI} values, can be further assessed.

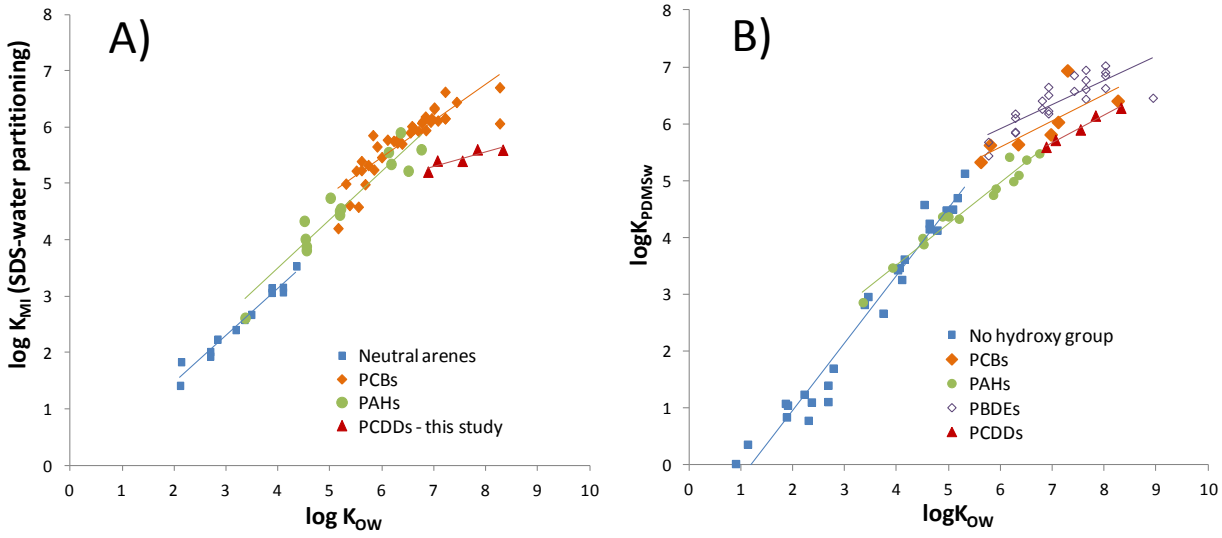

Figure 1. A) Relationship between log K_{OW} and log K_{MI} (for surfactant, SDS; data presented for K_{MI} on a M^{-1} basis, recalculated for the current study assuming a molecular weight for SDS of 288 g/mol); and B) K_{PDMS-W} for a range of neutral compounds. Data sourced from Dulfer et al[2], Rahman et al[8], Kim and Kwon[9], Almgren et al[10], Endo et al[11], Kwon et al[5], ter Laak et al[12], Escher et al[13], Escher (unpublished data).

The values for K_{MI} determined in this study for PCDDs suggest that the relationship between K_{MI} and K_{OW} may change for compounds of extreme hydrophobicity compared to similar compounds which are less hydrophobic; i.e. the relative increase in K_{MI} is lower than for K_{OW} as hydrophobicity increases (Figure 1A). Few property-property relationships for SHOCs and surfactants have been reported in the literature; however, Dulfer et al[2] and Rahman et al[8] observed lower K_{MI} values for partitioning of PCB 209 (log K_{OW} of 8.26) to SDS relative to its

partitioning to octanol, compared to the less hydrophobic PCB congeners (PCB 209 lies below the orange line representing a linear fit for lower chlorinated PCB congeners, Figure 1A). No other partitioning coefficients have been reported for compounds of log K_{OW} greater than 6.9 to SDS, and further data are required to establish whether this relationship generally holds for SHOCs or whether this is an experimental artifact related to the physico-chemical properties of these compounds. Hypotheses have been proposed which may account for a change in the K_{MI}-K_{OW} relationship for extreme hydrophobics partitioning to surfactants. Dulfer et al[2] proposed that the influence of the polar headgroups of the SDS micelles to screen the hydrophobic micelle core may be greater for more hydrophobic compounds, thus reducing the partitioning potential with increasing hydrophobicity. Alternatively, the more structured nature of surfactant micelles may require relatively more energy to form cavities compared to *n*-octanol and thus result in lower partition coefficients to micelles for larger and more hydrophobic molecules[2].

There is a general paucity of partitioning data for SHOCs to surfactant micelles and the method presented in the present study provides a promising approach for future experimental studies. In particular, the low replicate variability and increased upload capacity associated with uploading SHOCs to PDMS fibres using a polymer-swelling solvent may provide a consistent and flexible approach for studies that require polymer dosing methods across a range of applications. This approach also allows these experiments to be performed with low volumes of PDMS and water (0.78 µl and 270 µl, respectively, in the present study), thus reducing SHOC losses to glassware and reducing experimental costs. Overall, this method has the potential to provide a simple, cost-effective and robust method for quantifying partitioning of SHOCs in surfactant-water systems.

The initial results from these experiments suggest a high transport potential of PCDDs with surfactant micelles. These results are consistent with the enhanced mobility of PCDDs reported from an accidental surfactant release site, where PCDDs were observed in the subsurface at depths of several metres and were hypothesised to have been transported with facilitating surfactants[1]. Given the potential risk of groundwater contamination by SHOCs at sites where surfactants are known to be released, experimental methods as described in this study are important to describe, and therefore predict, the partitioning behavior of these extremely hydrophobic compounds.

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