Development and evaluation of a new diffusive gradients in thin-films technique for measuring organotin compounds in coastal sediment pore water

Russell F. Cole, Graham A. Mills, Michelle S. Hale, Ruth Parker, Thi Bolam, Peter R. Teasdale, William W. Bennett, Gary R. Fones

Abstract

Organotins present a toxicological risk to biota in the aquatic environment. Understanding the behaviour of these compounds in sediment is challenging, with sophisticated analytical techniques required for their measurement. We investigated the use of silica-bound sorbents for diffusive gradients in thin-films (DGT) adsorption gels to pre-concentrate five organotins (monobutyltin (MBT), dibutyltin (DBT), tributyltin (TBT), diphenyltin (DPHT), triphenyltin (TPhT)) found frequently in coastal sediment. C8 sorbent showed optimum performance in uptake and recovery of organotins for pH and ionic strength ranges typical of coastal waters. Recoveries from adsorption gels deployed in filtered sea water were MBT = 123 ± 20%, DBT = 75 ± 12%, TBT = 81 ± 16%, DPHT = 72 ± 30%, TPhT = 58 ± 10% respectively. Devices were used to investigate DGT fluxes and pore water concentrations of organotins in coastal sediment collected from a contaminated site. DGT fluxes measured in sediment cores for the five organotins ranged between 4.3 × 10^{-6} and 1.6 × 10^{-5} ng cm^{-2} s^{-1}. The depletion of organotin species within pore waters at the interface with DGT devices was measured over a series of deployment times (2, 7, 14, 21 and 28 days) and provided estimates of the concentration of organotins in pore waters at Langstone Harbour, UK, prior to depletion by the DGT device and information on their spatial heterogeneity. The novel in situ DGT device developed can pre-concentrate organotins from pore waters in coastal sediment core samples and allows their detection at low environmental concentrations using conventional gas chromatographic/mass spectrometric instrumentation. Use of the DGT device overcomes many problems associated with the conventional pore water sampling of organotins. Our preliminary data suggests it has potential in the future to be a useful tool in investigating the environmental fate of these pollutants. The use of the C8 gel will also allow for the simultaneous sequestration of other semi- and non-polar analytes present in the pore water.

1. Introduction

Organotins are the most widely used organometallic compounds globally (~50,000 t yr^{-1}) [1] with applications in the stabilisation of plastics, precursors in glass coating and as antifungal agents in textiles and other household items [2]. From the 1950s-2001, the major use of tributyltin (TBT) and triphenyltin (TPhT) was as a toxicant in anti-foulant paints [2]. Due to their high toxicity to non-target organisms [3–6] and persistence in the aquatic environment (half-life of TBT > 10 years in anoxic marine sediment, degrading to dibutyltin (DBT) and monobutyltin (MBT)), use of these compounds as antifoulants is now banned under the International Convention on the Control of Harmful Anti-fouling Systems on Ships [7]. Despite this ban, many coastal and marine sediments remain contaminated with TBT and other organotins, and therefore the management of such sediments remains an issue for policy makers and regulators.

Adsorption of organotins to sediment involves hydrophobic partitioning (a function of their log K_{ow}) and electrostatic interactions, which are related to the natural organic matter content and the abundance of negatively charged surfaces (e.g. deprotonated hydroxyl...
groups [8–10]. As a result, MBT, DBT, TBT, monophenyltin (MPbT), diphenyltin (DPhT) and TPhT have a high affinity for sediments and suspended particulate matter. Under certain conditions, however, these compounds can be desorbed into the aqueous phase [11]. Investigations on the mobilisation of organotins from contaminated sediment cores have been undertaken using core-slicing and pore water extraction by centrifugation, or by using natural/radiolabelled compounds in mesocosm [11,12] or microcosm [13–15] experiments. Although these approaches provided information on the partitioning and fate of organotins, they are intrusive and can produce artefacts such as changes to speciation and precipitation or adsorption of analytes to sampling apparatus [16]. To better understand the environmental behaviour of organotins within sediment pore waters, especially within the constraints of monitoring programmes, alternative methods are required.

Dialysis peepers have been used to measure MBT, DBT and TBT in coastal sediment pore waters [17], however, expensive instrumentation (e.g. solid-phase microextraction-gas chromatography-inductively coupled mass spectrometry (SPME-GC-ICP-MS)) is needed to detect analytes present in the small volumes obtained with this method. The use of passive sampling devices (PSDs) has received interest for measuring pollutants present in the water column at low concentrations (~ng L\(^{-1}\)) [18], including TBT (e.g. using semi-permeable membrane devices, silicone rubber sheets, Chemcatcher) [18–20]. Similar approaches have been used to measure pore water concentrations of non-polar organic compounds (e.g. DDTs, PAHs, PBDEs, PCBs) [21–24].

The diffusive gradients in thin-films (DGT) technique has been used previously for measuring labile metals [25], organometallics (e.g. methylmercury) [26] actinides, [27] oxyanions [28,29] and some polar organic compounds [30]. Conventional DGT comprises three layers: (i) a layer containing a resin with a functional group(s) selective for the target analyte/s supported within a thin hydrogel matrix; (ii) a layer of hydrogel of known thickness that restricts mass transport of the analyte through the gel to diffusion only, known as the diffusive layer; and (iii) a protective outer membrane of known thickness and pore size [25,31]. Manipulation of the pore size of the diffusive gel allows for the differentiation of non-complexed and organically associated metal species during simultaneous DGT deployments [32]. During deployment, analytes diffuse through the hydrogel layer at a defined rate (the diffusion coefficient) and are immobilised within the binding gel [32]. After retrieval, analytes are eluted from the binding gel and the mass accumulated determined [25]. The average flux to the binding gel and concentration of the analyte in the aqueous medium over the deployment time can then be determined [25]. In sediments, however, DGT does not directly measure the concentrations of analytes in bulk pore waters (C\(_{Pb}\)), but rather the mean concentration (C\(_{DGT}\)) at the surface of the device during deployment. The relationship of C\(_{DGT}\) to C\(_{Pb}\) depends upon the resupply of the analyte from the solid-phase to solution. Further explanation of this relationship and the dependence on the extent of resupply, is given in Harper et al. [33,34], Davison et al. [35] and Zhang et al. [36].

Here we describe the development of a novel DGT method, comprising of an octylsilyl (C\(_8\)) adsorption layer, suitable for measuring fluxes and interfacial concentrations of MBT, DBT, TBT, DPhT and TPhT in coastal sediment pore waters. Following deployment of DGT probes in coastal sediment cores (collected from Langstone Harbour, UK) and their analysis, sediment pore water depletion rates were fitted against regression models to estimate initial concentrations of organotins in pore water (before perturbation by the DGT devices). This new approach to interpreting DGT data has potential to further our understanding of the behaviour of organotins in situ and could be used as a tool to aid in monitoring, risk or impact assessments at coastal and open sea sites used for the disposal of contaminated dredge material from ports or harbours.

2. Experimental

2.1. Chemicals, reagents and standards

Chemicals were of analytical grade or better (Fisher Scientific Ltd., Loughborough, UK) unless otherwise specified. Organotin compounds are toxic and harmful to the environment, requiring care in use [37]. Sodium tetraethylborate (NaBEt\(_4\)) is spontaneously flammable in air and produces toxic fumes when added to water. Deionised water (> 18.2 M\(\Omega\) cm, Purite Ltd., Thame, UK) was used for all experiments and for cleaning. Plastic materials (including DGT bodies) and glass plates, used for preparing gels, were washed in Decon 90 (80 °C), soaked (24 h) in HCl (10%, v/v), rinsed with methanol and then water prior to use [38]. Mixed-cellulose ester (MCE) membranes (0.015 cm thickness and 0.45 µm pore-size; Millipore, Watford, UK) were washed in HCl (10%, v/v) for 24 h, rinsed with water and stored in NaCl (0.7 M). Information on the preparation of standards, reagents and buffers is provided in the Supporting information (Section S1 and S3).

2.2. Preparation of DGT adsorption gels

Preparation of diffusive gels (1.5% agarose, 0.05 cm thickness) is described in the Supporting information (Section S2). End-capped Bondesil\(^*\) C\(_8\) and C\(_{18}\) (both irregular shaped 40 µm, pore size = 60 Å) silica particles (Crawford Scientific, Strathaven, UK) were selected as potential DGT adsorption gel sorbents. These were used as either C\(_8\) or as an equivalent 50:50 mixture of C\(_8\) and C\(_{18}\), taking into account their differences in molecular weight. This resulted in a 1.0% C\(_8\) and 0.5% C\(_{18}\) by mass in the DGT adsorption gel. These sorbents are hydrophobic and require preconditioning before use. The procedures for making binding gels [39] were adapted for adsorption gels; with gels made from 40% acrylamide/bisacrylamide (BPA) (Sigma-Aldrich, Poole, UK) water and with the addition of methanol at 3:1:1 (v/v/v). Further details are provided in the Supporting information (Section S2).

The catalyst was N,N,N',N'-tetramethylethylenediamine (TEMED) and was used with a freshly prepared solution of 10% ammonium persulphate as the initiator for polymerisation. The pre-conditioning of sorbents was undertaken by soaking in methanol (~30 min). Sorbents were mixed into the gel solution using a magnetic stirrer and were cast by pipetting between 200 × 70 mm glass plates, separated using 0.05 cm acetate spacers. Gels were left to set flat in a fume hood for ~20 min. Adsorption gels were stored in water (4 °C) and were washed thoroughly prior to use. Cast gels were either cut to the dimensions of the DGT sediment probes or punched as 47 mm disks. The latter were used to compare their performance against C\(_8\) and C\(_{18}\) 3 M Empore\(\) disks (47 mm) (see Section S8.1 in Supporting information). Use of C\(_8\) and mixtures of this sorbent at masses higher than ~1% in the gel were too hydrophobic to allow for their satisfactory casting.

2.3. Uptake and elution efficiency of organotin on DGT adsorption gels

Uptake efficiency experiments (n = 3) were undertaken with C\(_8\) and mixed phase (C\(_8\)C\(_{18}\)) sorbents cast as 47 mm disks. Forty mL Oakridge\™ fluorinated ethylene propylene (FEP, a polymer with similar properties to PTFE, but is transparent) tubes (Fisher Scientific Ltd.) were used for the tests. Forty mL of organotin spiked solutions (2000 ng L\(^{-1}\)) were prepared using 0.001 M of the pH buffer (4–9) and/or 0.01–1.0 M NaCl in deionised water (see Section S3 Supporting information). Sodium chloride has been found to suitably mimic the properties of sea water in respect to “salting out” of hydrophobic compounds [10] and, therefore, was chosen for use in the ionic strength experiments. Uptake and elution efficiency tests were also undertaken in filtered (47 mm cellulose nitrate, 0.45 µm pore-size filters (Merck Millipore Ltd, Watford, UK) sea water (pH 8.0 and salinity 35) collected at Portsmouth Harbour, Hampshire, UK. Sea water samples were also spiked to a nominal concentration of 2000 ng L\(^{-1}\) for each organotin analyte.
To assess the performance of the adsorption gels at different concentrations, exposures were carried out between 500 and 5000 ng L\(^{-1}\) (for each organotin compound) at 0.01 M NaCl, pH 4.0. This pH was chosen as experiments showed that losses of organotins to the FEP tube were reduced at this value (Fig. S3 in Supporting information).

Uptake and elution efficiencies (%) were determined by mass balance, with the elution efficiency (%) calculated from the total mass of organotin (ng) in the sorbent Bondesil\(^\text{®}\) adsorption gel and also the mass in solution (ng, before and after phase exposure). The uptake efficiency (%) of organotin compounds was undertaken by the mass balance of solutions only. Spiked solutions with no gels were run for each experimental variable and were used to monitor changes in organotin-ligand partitioning behaviour, degradative losses and the adsorption of analytes to the FEP centrifuge tube wall. Bondesil\(^\text{®}\) gels were exposed for 48 h on an orbital shaker (240 rpm in the dark). Organotins were eluted from the adsorption gel for 24 h (240 rpm in the dark) into pre-cleaned FEP Oakridge\(^\text{™}\) tubes using methanolic acetic acid (13 M, 20 mL). The performance of adsorption gels in comparison with 47 mm, 3 M Empore\(^\text{®}\) disks is discussed in Section S8.1.1, Supporting information.

2.4. Determination of DGT diffusion coefficients

Experiments to determine diffusion coefficients of organotins were undertaken prior to the deployment of DGT devices in sediment, therefore, adsorption gel disks (47 mm) were overlain with a 0.05 cm thick agarose diffusive gel and a MCE membrane (0.015 cm thick, 0.45 µm pore size) in a custom made PTFE housing (AT Engineering, Tadley, UK). DGT diffusion coefficients (D) were determined in a glass tank (20 L) for 96 h, containing NaCl, (0.7 M, pH of 8.1 ± 0.1) solution so as to mimic the ionic properties of sea water [10]. The solution was spiked to a nominal concentration of 50,000 ng L\(^{-1}\) for each organotin compound and maintained at 20 °C. Due to the non-polar nature of analytes, experiments were undertaken at high concentrations to: 1) minimise the adsorption effect of organotins on to the glass wall of the tank, and 2) provide masses detectable in 10 mL solutions that were extracted for monitoring conditions in the tank. Further details are given in Supporting information (section S4). From the time series deployments, the mean mass (M, ng of organotin cation) of each compound was used to calculate D using Eq. (2) in Section 2.7.

2.5. Assembly and deployment of DGT devices

DGT devices were constructed in a laminar flow cabinet. Custom made Perspex\(^\text{®}\) DGT housings (AT Engineering) were used for the sediment probes. To reduce the deployment time of probes in sediments and yield masses detectable on the adsorption gel by GC/MS (Section 3.4), the agarose diffusive gel layer was removed from the device. Acetate spacers (159 × 39 mm) were placed behind the adsorption gel in order to bring the configuration forward in the housing. Adsorption gels, cut to the same size, were placed on the acetate platform, with the sorbent material uppermost in the cast gel (Fig. S2, Supporting information). The MCE membrane (159 × 39 mm) was rinsed with water and placed over the adsorption gel surface, ensuring no air was trapped between the two layers. The upper sampling window was then screwed securely in place using nylon screws.

For direct comparison of the kinetics and lability of organotins over time, measurements of organotin sediment-sampler kinetics were undertaken in ex-situ cores at 20 °C, ensuring constant submersion of DGT devices and the absence of site dynamic effects during deployment [25]. Five sediment cores were collected at low tide adjacent to a boating marina located at Langstone Harbour, UK (50 48 23′N, 00 55 12′W). Previously, sediments in this area were shown to be contaminated by TBT (~ 1300 ng g\(^{-1}\) dry weight) (Table S1 in Supporting information). Cores were collected with push-tube cores (30 cm long × 8 cm diameter) and were then sealed at the bottom with a clean rubber bung. Core samples were topped up with sea water from the sampling site, sealed at the top and transported to the laboratory within 1 h of sampling. Core samples were placed in the dark (20 °C) immediately after sampling and the overlying water was continuously aerated for the duration of experimentation. Prior to use, DGT devices weredeoxygenated with N\(_2\) for a minimum of 12 h. Devices were inserted into each core, ensuring a minimum of 2 cm of the sampling window was above the sediment water interface (SWI), and were removed individually at 2, 7, 14, 21 and 28 days. Once retrieved, the MCE membrane was discarded and the adsorption gels carefully removed. The adsorption gels were placed on to a plastic strip marked at intervals of 1 cm (giving an area = 1.9 cm\(^2\)). Gels were cut using a Teflon™ coated razor blade and were eluted using methods described in Section 2.6.

2.6. Analysis

Adsorption gels were eluted with methanolic acetic acid (20 mL, 13 M) into 40 mL Oakridge FEP tubes and extracted for 24 h on an orbital shaker (in the dark at 240 rpm). Gel extracts were transferred to a volumetric flask (100 mL), the FEP tube and gel rinsed with methanol (20 mL), and the solutions and rinsate combined for derivatisation. The eluate in the flask was adjusted to pH 4.20 ± 0.1 using 10 mL, 20% NaOH (w/v) and 1 M sodium acetate buffer solution (10 mL). Fifty µL (50 ng) of tripropyltin chloride (TPrTCl) internal standard was added to the solution which was then made up to 100 mL using methanol. One % NaBF\(_4\) (1 mL) was used to ethylate organotins and was undertaken by simultaneous extraction and derivatisation into 2 mL n-hexane (using a mechanical flask shaker for 15 min). Extracts were allowed to settle for ~ 30 min. The n-hexane layer was removed and 1–2 g sodium sulphate added to the extract to remove any excess water. For mass balance solutions (uptake and elution efficiency of organotins on DGT adsorption gels), 10 mL of water (before uptake) and 30 mL of the post uptake solution were transferred to a volumetric flask (250 mL). The pH of solutions was adjusted to 4.20 ± 0.1 using 1 M sodium acetate buffer solution (1 mL) and was simultaneously derivatised and extracted into n-hexane (2 mL). Organotins were measured using pressure temperature vapourisation-large volume injection (10 µL injection volume) gas chromatography-mass spectrometry (PTV-LVI-GC/MS) operated in the selective ion monitoring mode [40] (see Supporting information section S7). Limits of quantification (LoQ) were calculated using the International Conference on Harmonisation method [41], where 10 times the standard deviation of the instrument response of the lowest calibration standard (σ) is divided by the slope (s) of the calibration curve (LoQ = 10σ/s). The LoQs, as organotin cation in final n-hexane extracts, were MBT = 2.4 µg L\(^{-1}\), DBT = 0.9 µg L\(^{-1}\), TBT = 0.7 µg L\(^{-1}\), DPhT = 1.3 µg L\(^{-1}\), TPhtT = 0.5 µg L\(^{-1}\).

2.7. Calculations

The mass accumulated on the adsorption gel (M, ng) was calculated from the concentration of organotin compounds in the n-hexane extract (C\(_n\), ng cm\(^{-3}\)), the adsorption gel volume (V\(_g\) = 0.096 cm\(^3\)), the volume of the n-hexane extract (V\(_e\) = 2 cm\(^3\)), and the elution factor(s) (f\(_e\)), determined from uptake and elution experiments (Eq. (1)).

\[
M = \frac{C_n(V_g+V_e)}{f_e}
\] (1)

By plotting the mean mass from adsorption gels removed at each time interval, the slope of organotin uptake was used to calculate (Eq. (2)) analyte diffusion coefficients (D, cm\(^2\) s\(^{-1}\)) [42], with diffusive gel layer and membrane thickness (A\(_g\)) of 0.065 cm [29]; sampling area for each 1 cm profile interval (A) of 1.9 cm\(^2\); and the average concentration of the uptake solution (C, µg cm\(^{-3}\)) during DGT deployment.
\[
D = \frac{\text{slope} \cdot \text{g}}{\text{CA}} \quad (2)
\]

For deployments in sediment, DGT flux \((J, \text{ng cm}^{-2} \text{s}^{-1})\) and the freely dissolved concentrations of analytes in interfacial pore water \((C_{\text{DGT}})\) were calculated using Eq. (3) for \(J\) and Eq. (4) for \(C_{\text{DGT}}\).

\[
J = \frac{M}{tA} \quad (3)
\]

\[
C_{\text{DGT}} = \frac{J \cdot \Delta g}{D} \quad (4)
\]

\[2.8. \text{Statistical analysis}\]

Data obtained from the different sorbent phase experiments were investigated for normality and homogeneity of variances (Levene's test). Where the assumptions of the test were met, a two-way ANOVA \((\alpha = 0.05)\) was used to compare mean elution and uptake efficiencies of organotins from the four separate phases across the ranges of pH, ionic strength and organotin concentrations tested. Tukey's post-hoc analysis was undertaken to determine where significant differences occurred. For data not meeting the assumptions of normality and homogeneous variances, a Kruskal-Wallis test was used and post hoc pair-wise comparisons were made using a Mann-Whitney \(U\) test. To determine which phase demonstrated the most consistent performance across all test variables, ionic strength and pH data sets were directly compared with each other using an independent samples \(t\)-test for each phase. Where there were no significant differences in mean elution efficiency \((\%)\) between the data sets, an overall elution efficiency for the phase was calculated using the mean of all data. Linear regressions were conducted to obtain DGT diffusion coefficients from the mass of organotins accumulated over time.

\[3. \text{Results and discussion}\]

\[3.1. \text{DGT adsorption gel}\]

Loading \((\%)\), sorbent distribution, ease of casting and effect of particle size \((\mu m)\) of \(C_8\) and \(C_{18}\) were investigated as part of the method development for the organotin DGT adsorption gel. The sorbents investigated were Bondesil® \(C_8\) (40 µm), Bondesil® \(C_{18}\) (40 µm), and Silicycle® \(C_8\) monomeric spherical sorbents \((5 \mu m)\) and Silicycle® \(C_{18}\) monomeric spherical sorbents \((5 \mu m)\). The best particle distribution and casting was found with 1% Bondesil® \(C_8\) (40 µm) and 1:0.5% \((w/w)\) Bondesil® \(C_8:C_{18}\) (40 µm) mixed-phase gels (see section S2 in the Supporting information), hence these were selected for further testing.

\[3.2. \text{Uptake and elution performance of adsorption gel}\]

Bondesil® \(C_8\) gels and Bondesil® mixed-phased gels showed no significant differences \((p > 0.05)\) in uptake and elution \((\%\) performance) across variations in concentration of organotins \((500–5000 \text{ng L}^{-1})\), pH 4–9, ionic strength \((0.01–1 \text{ M, NaCl})\) and in filtered sea water samples. These data are shown in Table 1 \((C_8\) gel) and Table S3 \((C_8:C_{18}\) gel). However, standard deviations \((\%)\) were found to be higher in comparison to DGT measurements using Chelex-100 [26] and o-DGT XAD-18 [31] binding and adsorption layers. The higher variability in the data were considered as a result of hydrophobic and electrostatic interactions and anisotropic adsorption effects of the organotins to FEP tube walls.

There was a difference in the adsorption behaviour of organotin solutions \(\text{(containing no gels)}\) to the walls of the FEP tube with pH. This effect predominated at pH ranges > 5 and at low analyte concentrations \((\text{Fig. S3 in Supporting information})\). When an adsorptive gel was added to the tubes a new equilibrium between the three compartments \((\text{gel, solution and tube})\) was established. This resulted in organotins partitioning from the tube wall into solution that were then available for uptake by the sorbent. This partitioning effect was attributed, in part, to causing some of the variability in the uptakes and subsequently measured recoveries of the organotins.

For filtered sea water samples, reproducibility was highest for all compounds \((\text{standard deviations between 2% and 30%})\), although the mass balance for MBT in the Bondesil® \(C_8:C_{18}\) mixed-phase gel was found to be unmeasurable \((\text{Table S3 in Supporting information})\). Bondesil® \(C_8\) adsorption gels showed no significant difference in mean elution efficiency \((\%)\) across pH, ionic strength concentrations and in filtered sea water samples \((p > 0.05)\) and mean elution efficiencies calculated from Bondesil® \(C_8\) adsorption gel data were; MBT = 105 ± 41%, DBT = 74 ± 26%, TBT = 104 ± 22%, DPhT = 67 ± 26% and TPhT = 66 ± 10%. Therefore, Bondesil® \(C_8\) (40 µm) was selected as the DGT adsorption gel phase as it showed the best casting performance \((\text{with the reduced hydrophobic influence of shorter n-alkane chains})\) and optimal uptake and elution efficiencies \((\%)\) across all the parameters tested. Adsorption gel and 3 M Empore® disk comparisons are discussed in Supporting information \((\text{Section S8.1})\).

\[3.3. \text{Linear uptake and DGT diffusion coefficients}\]

Devices were removed from the tank in triplicates and the mass \((\text{M})\) on adsorption gels determined by methods in Sections 2.6 and 2.7. The mean values of mass \((\text{ng of organotin cation})\) were calculated at each time interval and were used to calculate the uptake diffusion coefficients of each analyte, as shown in \((\text{Eq. (2)}, \text{Section 2.7})\). A linear uptake of analytes was observed during the first 72 h of sampling, with 96 h deployments showing a departure from linearity \((\text{Fig. 1})\) and a loss of mass for the butylin compounds. Two explanations were considered: (1) the capacity of the adsorption gel had been reached, with the decrease in mass caused by adsorption site competition with other analytes \(\text{(e.g. MPbT, which was not included in the DGT analyte suite})\); and (2) the anisotropic adsorption of organotins to the \(C_8\) phase, where adsorption gels had reached equilibrium with the dissolved phase, causing the partial offloading of butylin back into solution in the tank \([20]\). After 72 h, phenyltins \(\text{(DPhT and TPhT)}\) showed an increased departure from linearity \((r^2 = 0.94–0.97)\) in comparison to the butyltins \((r^2 = 0.99)\), with no distinguishable loss of mass at 96 h. It was hypothesised that this was indicative of phenyltin compounds showing a difference in pore water-sampler uptake kinetics, although elucidating the exact mechanism of this was beyond the scope of this study.

\[\begin{array}{|c|c|c|c|c|c|}
\hline
\text{pH at} & \text{MBT} & \text{DBT} & \text{TBT} & \text{DPhT} & \text{TPhT} \\
\text{NaCl} & \text{0.01 mol L}^{-1}\text{ at pH 8} & & & & \\
4 & 104 ± 58 & 72 ± 17 & 102 ± 14 & 73 ± 18 & 66 ± 3 \\
5 & 102 ± 44 & 85 ± 5 & 93 ± 19 & 74 ± 6 & 62 ± 6 \\
6 & 97 ± 36 & 122 ± 7 & 64 ± 17 & 79 ± 12 & \\
7 & 101 ± 16 & 74 ± 25 & 102 ± 3 & 63 ± 18 & 75 ± 9 \\
8 & 81 ± 15 & 103 ± 46 & 92 ± 25 & 59 ± 22 & 62 ± 10 \\
9 & 68 ± 43 & 65 ± 14 & 125 ± 19 & 38 ± 27 & 65 ± 11 \\
\hline
\end{array}\]

\[\text{Table 1}
\text{Mean recoveries (\%) of organotin compounds from Bondesil® \(C_8\) adsorption gel over ranges of pH 4–9, ionic strength (NaCl 0.01–1.0 mol L}^{-1}\) and in filtered sea water \((n = 3)\). SD = standard deviation. Abbreviations for organotin compounds as in text.}\]
For 0–72 h, butyltin compounds had $r^2$ values of 0.99 or higher (Fig. 1). Using Eq. (2) (Section 2.7), DGT diffusion coefficients ($D$) (n = 3) for organotins in a solution of NaCl (0.7 M) at pH 8.0 (20 °C) were (mean ± SD): MBT = $8.71 \times 10^{-6}$ (± 2.80 × 10$^{-6}$), DBT = $4.68 \times 10^{-6}$ (± 2.13 × 10$^{-6}$), TBT = $7.49 \times 10^{-6}$ (± 7.22 × 10$^{-7}$), DPhT = $5.70 \times 10^{-6}$ (± 8.48 × 10$^{-7}$) and TPhT = $4.22 \times 10^{-6}$ (± 9.09 × 10$^{-7}$) cm$^2$ s$^{-1}$.

There is a paucity of data on diffusion coefficients of organotins, with few authors reporting values for MBT, DBT, DPhT and TPhT. Smedes and Beeltje [19] measured diffusion coefficients of organotins through silicon rubber sheets and report values of $D$ for butyl and phenyl tin compounds of 2.7 × 10$^{-9}$ to 1.2 × 10$^{-10}$ cm$^2$ s$^{-1}$. Hamer and Karius [43] reported $D$ values of 2.92 × 10$^{-6}$ to 4.92 × 10$^{-6}$ cm$^2$ s$^{-1}$ for TBTOH in natural water under estuarine conditions (12–20 °C). Values of $D$ for TBT measured in the current study (between 1.5% agarose gel and MCE membrane, 0.45 µm pore size) were higher than those measured in silicon rubber sheets, and were similar to those measured in water, indicating that the DGT assembly did not significantly retard the free diffusion of analytes to the adsorption gel.

3.4. DGT flux and interfacial pore water concentrations

The 1.5% agarose gel had a pore size > 20 nm [44], with its composition and diffusive properties similar to those of water [45,46]. Due to the low energy conditions of sediments, the free diffusion of organotins from sediment pore water through the gel and the MCE membrane layer (0.065 cm) was expected to require extended deployment times to achieve detectable masses on the adsorption gels for detection by GC/MS. Subsequently, the removal of the agarose diffusive layer was undertaken and the values of $D$ (Section 3.3) were used to calculate interfacial pore water concentrations, but with the thickness corrected in Eq. (4) to that of the MCE membrane only ($\Delta g = 0.015$ cm). All sampling was undertaken at 20 °C, therefore, changes to diffusion coefficients using the Stokes-Einstein equation were not required [27,44]. Fig. 2 shows the DGT flux ($J$, ng cm$^{-2}$ s$^{-1}$) and the concentrations of organotins in interfacial pore waters ($C_{DGT}$, ng L$^{-1}$) at 1 cm resolution(s), for deployments of 2–28 days.

Using non-deployed DGT sediment probes (blanks) and GC/MS limits of detection, the method detection limits (MDLs) for DGT $C_{DGT}$ (as ng L$^{-1}$) for deployment times were calculated from the lowest absolute mass (M, ng) detectable on the adsorption gels. DGT detection
limits for TBT at 2 weeks deployment (0.4 ng L\(^{-1}\)) were comparable to those reported using PTV-LVI and perdeuterated standards in 50 mL centrifuged pore water extracts\[9\]. A summary of the absolute detection limits (M, ng) and the CDGT method detection limits (MDL, ng L\(^{-1}\)) for different deployment times is given in Table 2.

DGT deployments showed a non-sustained uptake scenario \[25,34,47\] with analyte depletion at the interfacial pore water of the sampler occurring within the 2–28 day experimental timeframe (Fig. 2). For the organotin compounds MBT, DBT, DPhT and TPhT, J and CDGT were found to have their highest values after 2 days (compared to the values obtained in the 1, 2, 3 and 4 week deployments). The more polar analytes (MBT and DPhT) had the highest mass sequestered on the adsorption gels (giving CDGT values in the range 12–48 ng L\(^{-1}\)). Due to reduced concentrations in pore water, TBT was not detected with a deployment of 2 days, with masses below the DGT detection limit with GC/MS (M = < 0.4 ng). After 1 week, adsorbed masses for TBT had increased to quantities detectable by GC/MS, however, DBT, DPhT and TPhT still had intervals of 1 cm depth(s) where masses were below their respective detection limits and were indicative of greater spatial heterogeneity compared to butyltin compounds (Fig. 2 and Table 2). After 4 weeks, DGT J and CDGT had reduced to their lowest measured ranges (Fig. 2), with organotin masses having an overall reduction from week 3 measurements. DPhT and TPhT ‘hotspots’ were detected in the week 4 profile at \( -2 \) and \( -8 \) cm depths, also indicative of phenyltin heterogeneity within sediment cores. By week 4, the concentration gradient

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**Table 2**

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<th>Analyte</th>
<th>Method detection limits (MDL) (ng)</th>
<th>CDGT MDL (ng L(^{-1}))</th>
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<td></td>
<td></td>
<td>Days of deployment</td>
</tr>
<tr>
<td>MBT</td>
<td>1.7</td>
<td>8.7</td>
</tr>
<tr>
<td>DBT</td>
<td>0.9</td>
<td>2.7</td>
</tr>
<tr>
<td>TBT</td>
<td>1.4</td>
<td>12.1</td>
</tr>
<tr>
<td>DPhT</td>
<td>1.4</td>
<td>7.3</td>
</tr>
<tr>
<td>TPhT</td>
<td>0.6</td>
<td>4.3</td>
</tr>
</tbody>
</table>

\[ a \] DGT deployment times demonstrating concentrations below CDGT MDL (ng L\(^{-1}\)).

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**Fig. 2.** DGT organotin flux (J) and interfacial concentrations (CDGT) in pore water from ex-situ coastal sediment cores from Langstone Harbour, Portsmouth, UK, over 2, 7, 14, 21 and 28 day deployments.
between the adsorption gel and pore water had diminished, with limited or no resupply of organotin compounds to the pore water phase occurring (a non-sustained DGT uptake scenario) [34,47]. The decrease in mass was likely caused by 1) the offloading of analytes back into the external sediment-water boundary layer (as a function of first order kinetics and the establishment of an equilibrium between the adsorption gel and the interfacial pore waters), and 2) competition from the simultaneous uptake of natural organic matter and other organic contaminants in the sediment during sampling. For other sediment PSDs, hydrophobic organic compound (HOC) passive samplers commonly operate under equilibrium regimes, as this provides more consistent measurements from longer deployment times [23]. As DGT operates under a kinetic sampling regime, the resolution between profile depth intervals decreased with deployment time. This was a function of DGT sampling a larger volume of water as it approached equilibrium (with concentrations determined as volume-weighted averages (VWA)) and was not considered a function of capillary resupply of organotins (with only a small fraction of pore water next to the sampling interface being depleted by the DGT sampler (Section 3.5)). Consequently, the VWA measurements at 2 and 7 days provided a much higher resolution of organotin DGT profiles in comparison to those determined at 21 and 28 days (Fig. 2) with the variability in the vertical profile attributable to the limited mass accumulated at these times. Increased mobilisation of MBT, TBT, DPhT and TPhT was observed in the 0–8 cm of the DGT profiles.

3.5. Sediment pore water concentrations at t = 0

One approach to estimate the concentration of an analyte in the pore water of sediment cores is to use different thicknesses of diffusive gels (Δg, cm). Here the mass of analyte obtained from a series of multiple deployments can be used to obtain an intercept value for 0 = 1/ Δg. This corresponds to the concentration before the system is perturbed by the insertion of the sampling device [34]. For this work, an alternative approach was used. In this case, concentrations of organotins in pore water at t = 0 (CDGT (t=0)) were estimated from measurements of Cfree in sediment cores, using data obtained from time-series deployments (2–28 days) (Section 3.4). This was achieved by plotting all CDGT data (at 1 cm resolution for all depths in the profiles) for each organotin against time (Fig. 3). There was heterogeneity in the data, this being more pronounced in the early deployment times (2 and 7 days). This was attributed to both inter- and intra-processes of the sediment cores. The inter-variability arose due to short lived sources (giving rise to peaks in the profile (Fig. 2)) of organotins within the sediment which were then depleted by their sequestration into the device after week 2. Afterwards (weeks 2, 3 and 4) these peaks of organotins then disappear from the profile due to the system not being fully sustainable with a constant re-supply of analyte [34,35]. As a result the data profile becomes more homogenous. In addition, there are likely to be intra-variability effects that can be attributed to the requirement to use different sediment cores in the time series experiment.

Data obtained from the time series deployments were fitted using different models of regression in Genstat®, with standardised residuals of the data used to establish the different depletion equations. These regression curves were then used to estimate CDGT (t=0) for each of the organotins (Fig. 3). For MBT (log Kow = 0.18) [19] and DPhT (log Kow = 1.38) [19], pore water depletion appeared to occur via two processes, being expressed as an exponential depletion curve with an added linear term, yielding y = A + Be-kt + Ct (where A = lower limit of the model, B = the intercept of the curve, C = rate of the linear component, k = the rate constant (day-1) and t = time (day)). The depletion of MBT and DPhT in pore water by DGT was considered to be a function of their polarity and the anisotropic adsorption kinetics associated with organotin compounds [20]. Furthermore, degradation of other organotin compounds present in the cores could potentially contribute to the resupply of MBT and DPhT from pore water. However, the extent of this resupply was not determined in this study. Data for DBT (log Kow = 1.89) [19] and TPhT (log Kow = 3.93) [19] was best fitted by a simple exponential equation (y = A + Be-kt). This function contains one kinetic term; this was considered indicative of a limited, non-sustained supply of these semi- and non-polar compounds at the DGT interface. The influence of the potential degradative conversion of TBT to DBT over the time course of the study could not be measured. The depletion of TBT from pore water gave a linear function (y = B - Ct). The uptake of TBT (log Kow = 4.70) [19] by DGT was the slowest (not detected after 2 days of deployment) for all compounds tested and was considered to be a function of its hydrophobicity.

Extrapolation of the five curves to the intercept value (t = 0) (Fig. 3), gave CDGT (t=0) for MBT = 21 ng L-1, TBT = 36 ng L-1, DPhT = 41 ng L-1 and TPhT = 12 ng L-1. It is difficult to compare these pore water concentrations to those available in the limited published literature due to differences in sediment heterogeneity and the method used to collect the sediment and isolate the pore water. Table S4 (Supporting information) shows concentrations of butyltins in pore water and total sediment samples collected from marine and fresh water sites. Our calculated pore water concentrations for the butyltins falls within the range of reported values.

The above regression equations were used to calculate CDGT (t=0) from just the CDGT values obtained from devices deployed at either 2, 7, 14, 21 or 28 days (Figs. S4 and S5, Supporting information). The estimated value of CDGT (t=0) was best fitted at t = 2 or 7 days, with the greatest departure from the modelled regression curves being observed in the longer term deployments. These data suggest that the calculation of CDGT (t=0) from a single DGT measurement is less reliable on an extended deployment time and that CDGT measurements nearer to t=0 yield more reliable estimates of the initial pore water concentration. Hence, the use of multiple time series deployments nearer to t=0 are recommended for the calculation of CDGT (t=0).

Research over the last 20 years has highlighted the usefulness of PSDs for analysis of pollutants in sediments [47–51]. Currently, PSDs are being used to investigate the environmental fate, bioaccumulation, and toxicity of HOCs [52] and metal behaviour and bioavailability [53,54] in sediments. The wide range of available PSDs and associated sensitive analytical methods have been a driver for advancement of this field. Future development is crucial, however, there needs to be a consensus on the appropriate use of PSDs to help support the management of contaminated sediments [52].

We have developed a new variant of DGT device that uses a Cg adsorptive phase in an acrylamide/bis-acrylamide gel used for the sequestration of five environmentally important organotins from sediment pore waters. Extrapolation of CDGT pore water depletion curves from the time series deployment regimes allowed for modelled estimates of organotin pore water concentrations CDGT (t=0) prior to sediment perturbation by the insertion of the DGT device into the core. CDGT (t=0) can be viewed as a proxy for the Cfree concentration obtained usually using HOC PSDs. Knowledge of the Cfree concentration is important in understanding the fate, transport, bioaccumulation and toxicity of hydrophobic pollutants. For organotin compounds being able to estimate the Cfree concentration is important for the environmental assessment of contaminated sediments and management of dredged material disposal sites.

As the Cg sorbent material is able to sequester a wide range of non- and semi-polar chemicals, the DGT device could potentially have wider applications in measuring such pollutants in pore waters of coastal and marine sediments.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2017.09.081.

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[7] International Maritime Organisation International Convention on the Control of
Harmful Anti-fouling on Ships. (Accessed 16th March).


