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

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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 (monobutlytin (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 = $123 \pm 20\%$, DBT = $75 \pm 12\%$, TBT = $81 \pm 16\%$, DPhT = $72 \pm 30\%$, TPhT = $58 \pm 10\%$ 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^{-8} and 1.6×10^{-5} ng cm² 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 antifoulant 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

monobutlytin (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

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groups) [8–10]. As a result, MBT, DBT, TBT, monophenyltin (MPhT), 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 meso-cosm [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 (\sim 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_b) , but rather the mean concentration (C_{DGT}) at the surface of the device during deployment. The relationship of C_{DGT} to C_b 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 (NaBEt₄) is spontaneously flammable in air and produces toxic fumes when added to water. Deionised water (> 18.2 MΩ 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[®] C₈ and C₁₈ (both irregular shaped 40 μ m, pore size = 60 Å) silica particles (Crawford Scientific, Strathaven, UK) were selected as potential DGT adsorption gel sorbents. These were used as either C8 or as an equivalent 50:50% mixture of C8 and C18, taking into account their differences in molecular weight. This resulted in a 1.0% C8 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'-tetramethylenediamine (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 \times 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 C8 and C18 3 M Empore® disks (47 mm) (see Section S8.1 in Supporting information). Use of C₁₈ and mixtures of this sorbent at masses higher than $\sim 1\%$ in the gel were too hydrophobic to allow for their satisfactory casting.

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

Uptake efficiency experiments (n = 3) were undertaken with C₈ and mixed phase (C₈:C₁₈) 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. Download English Version:

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