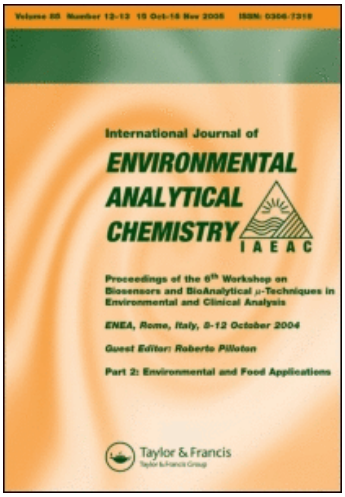

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Aguilar-Martínez, Rocio , Greenwood, Richard , Mills, Graham A. , Vrana, Branislav , Palacios-Corvillo, Maria A. and Gómez-Gómez, Maria M.(2008) 'Assessment of Chemcatcher passive sampler for the monitoring of inorganic mercury and organotin compounds in water', International Journal of Environmental Analytical Chemistry, 88: 2, 75 — 90
To link to this Article: DOI: 10.1080/03067310701461870
URL: http://dx.doi.org/10.1080/03067310701461870

Intern. J. Environ. Anal. Chem.
Vol. 88, No. 2, 15 February 2008, 75–90

Assessment of Chemcatcher passive sampler for the monitoring of inorganic mercury and organotin compounds in water

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(*Received 29 March 2007; in final form 17 May 2007*)

Several configurations of receiving disks and diffusion membranes were tested for monitoring mercury and organotin compounds (monobutyltin, dibutyltin, tributyltin, and triphenyltin) in water with a passive sampler. This passive sampler is based on the diffusion of these compounds through a specific diffusion-limiting membrane and their subsequent accumulation on a specific receiving phase, all materials being commercially available. The proposed sampler for inorganic mercury comprises a 47-mm Empore^{TM} chelating disk as receiving phase and polyethersulfone as diffusion membrane. For monitoring organotins, the receiving phase is a 47-mm Empore^{TM} C_{18} disk, and the diffusion membrane is cellulose acetate. ICP-MS and GC-ICPMS/GC-FPD were used for inorganic mercury and the organotins analysis, respectively. The effects of environmental variables such as pH and salinity that could influence accumulation of test substances in receiving phase were studied. Linear uptake for all compounds was observed for at least 14 days of exposure at a constant aqueous analyte concentration in a flow-through system under controlled conditions of temperature, turbulence, and analyte concentration. Compound-specific sampling rates at 11°C and simulated water turbulence of 40 cm s^{-1} varied between 0.018 and 0.137 L d^{-1}. Compounds collected by the sampler exhibited detection limits ranging between 0.7 and 5.9 ng L^{-1}. The feasibility of using these samplers in the field was tested in a polluted commercial harbour. The behaviour of the samplers to monitor target compounds was compared with those obtained from spot samples of water taken throughout the field deployment period. Data from laboratory studies and field trial support the feasibility of these samplers to measure the freely dissolved fraction of these important target analytes in water.

Keywords: Water monitoring; Passive sampling; Chemcatcher; Mercury; Organotin compounds; GC-ICP/MS

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International Journal of Environmental and Analytical Chemistry
ISSN 0306-7319 print/ISSN 1029-0397 online © 2008 Taylor & Francis
DOI: 10.1080/03067310701461870

1. Introduction

Mercury and organotin compounds [monobutyltin (MBT) dibutyltin (DBT), tributyltin (TBT) and triphenyltin (TPhT)], because of their accumulative properties and toxic effects in both aquatic organisms and humans, have been included in the list of priority environmental pollutants of European Union (water Framework Directive 2000/60/EC). The maximum permissible total mercury concentration in drinking water is $2\,\mu g\,L^{-1}$ (US EPA). For the organotin compounds, the WHO guidelines give a value of $10\,ng\,L^{-1}$ for TBT in seawater [1, 2]. The development of methodologies for both the field sampling and instrumental analysis of these substances in water is paramount. However, this is a difficult task because there are many potential factors influencing their monitoring and analysis. The challenges include the attainment of the methodological and instrumental sensitivity necessary for the determination of the low concentrations found in environmental samples; the preservation of the identity of species or the achievement of simple, inexpensive, and robust monitoring procedures.

Currently, the prevalent method of monitoring pollutants in the aquatic environment is based on the collection of spot (bottle or grab) samples. However, spot sampling suffers from several disadvantages: (1) it yields only an instantaneous measurement of pollutant levels at the time of sampling; (2) losses of analytes can occur during the transport of samples to the laboratory and during their subsequent storage prior to analysis; (3) the addition of preservative agents to prevent losses due to adsorption and volatilization increases the risks of sample contamination and/or chemical transformation of test species; and (4) large sample volumes (about 1 L) need to be collected because of the low concentration of pollutants of interest in many water systems. Furthermore, in most cases, a pre-concentration step is necessary for the analysis of mercury and organotin compounds in order to achieve the instrumental detection limits for their determination [3–5]. The instrumental techniques used include flow injection cold vapour atomic fluorescence spectrometry (FI-CV-AFS) for mercury, gas chromatography coupled to a flame photometric detector (GC-FPD) and gas chromatography coupled to an inductively coupled plasma-mass spectrometer (GC-ICP-MS) for organotin compounds [6, 7].

An alternative monitoring strategy is provided by biomonitoring where the bioaccumulation of pollutants in living organisms is used as a measure of concentrations of pollutants in the water [8–10]. However, this approach has several drawbacks; for example, the rate of bioaccumulation varies between both test species and individuals, and organisms can metabolize and depurate test pollutants [11].

Passive sampling is a promising alternative monitoring method. It enables the measurement of the mean water concentration (C_w) of a compound over the deployment period to be estimated. Amounts accumulated by passive sampling reflect the concentration of the freely dissolved or labile fractions which are generally assumed to be the most bioavailable of target compounds in water. In contrast, the fraction of a pollutant bound to suspended matter or dissolved organic carbon (DOC) is generally not accumulated by these types of samplers [12]. Most designs of passive sampler consist of a receiving phase with a high affinity for the pollutants of interest, separated from the external aquatic environment by a thin diffusion membrane [12].

There are an increasing number of available passive sampling systems for monitoring water quality, but most of them have been developed for non-polar compounds with a $\log K_{ow}$ greater than 4, and very few have been developed for metals and organometals.

For organotin compounds, the triolein filled SPMDs performed well in monitoring the soluble (bioavailable) fraction mainly for TBT [10]. For mercury, two devices have been described: the passive integrative mercury sampler (PIMS) applicable to monitoring of neutral vapour and dissolved neutral mercury (Hg^0) species [13], and the diffusion gradient in thin films (DGT) for ionic mercury [14, 15]. Other examples of passive samplers for metals are: the stabilized liquid membrane device (SLMD) for sequestering toxic metal ions [16], the permeation liquid membrane (PLM) sampler for monitoring Cd and Pd [17], and the Ecoscope for several trace elements including inorganic mercury [18].

Kingston *et al*. [19] and Persson *et al*. [20] previously developed a novel passive sampler, identified as the Chemcatcher, for the measurement of mean water concentrations of a range of pollutants (including both non-polar and polar organic compounds and a range of heavy-metal ions) in different aquatic environments. The system is based on the diffusion of target compounds through a diffusion membrane and their subsequent accumulation in a solid receiving phase. The accumulation rate and selectivity of the device for the different pollutant classes are regulated by the choice of both the diffusion-limiting membrane and the solid-phase receiving material used.

In this article, a suitable combination of receiving phase and diffusion membrane materials for Chemcatcher samplers have been studied for the monitoring of inorganic ionic mercury and organotin species in water. The effects of water pH, salinity, and biofouling have been evaluated. The performance of the devices has been tested in a pilot field trial at a polluted marine site in Spain.

2. Experimental

2.1 *Chemicals and reagents*

All reagents were of analytical grade or better purity. Ultrapure Milli-Q water (Millipore, OH) was used to prepare all test solutions. Standard stock solutions (1000 mg L^{-1}) of inorganic mercury chloride, the organotin chloride compounds MBT, DBT, TBT, and TPhT, and the internal standard tripropyltin (TPrT) (Alfa Aesar, Karlsruhe, Germany) were prepared by dissolving appropriate amounts in 1% nitric acid (65% w/v Merck, Darmstadt, Germany) for mercury and in methanol (SDS, Barcelona) for organotin species. All stock solutions were stored in amber glass bottles at 4°C in the dark. Working solutions were prepared by appropriate dilution of the stock solutions.

A 0.24 mol L^{-1} distilled hydrochloric acid (37% w/v, Scharlab, Barcelona) solution was used as ICP-MS carrier for inorganic mercury detection. An aqueous solution (1% w/v) of sodium tetraethylborate (98% w/w, Strem Chemicals, Bisheheim, France) was used as a derivatizing agent in a 2 mol L^{-1} acetic-acetate buffer (pH 4.6). This buffer was prepared by dissolving the appropriate amount of sodium acetate (99% w/w, Merck, Darmstadt, Germany) in acetic acid (99% w/v, Scharlab, Barcelona) and Milli-Q water to give the final volume.

Artificial seawater was prepared by dissolving 33.35 g of seawater salt (HW Professional, Spain) in 1 L of tap water. The artificial seawater had been checked previously for the presence of mercury and organotin species. The effect of pH was

studied by the addition of HNO_3 or NaOH to tap water until the desired pH was achieved.

2.2 *Materials and apparatus*

2.2.1 Receiving components and membranes. C_{18}, cation exchange (SDB-RPS) and chelating (CHE) Empore^{TM} disks (47 mm in diameter) were obtained from 3M (Bioanalytical Europe, Neuss, Germany). Polyethersulfone (PS) (Z-Bind^{TM} 0.2 μm pore size) and cellulose acetate (CA) (0.45 μm pore size) were purchased from Pall Europe (Portsmouth, UK); low-density polyethylene (PE) (10 Å pore size) was from Fischer Scientific (Loughborough, UK); and cellulose dialysis membrane (D) (3500 molecular-mass cutoff) was from Spectra/Por^{TM} 3 (Spectrum Europe V, Breda, The Netherlands).

2.2.2 Flow-through exposure tank. The flow-through exposure tank used for the laboratory experiments was similar to that described by Vrana *et al.* [21]. It consisted of a 24-L glass tank ($31.5 \times 38 \times 40$ cm) with an overflow to waste. Tap water and the solution of test analytes were pumped into the exposure tank separately at known and controlled rates. Water was fed using a peristaltic pump (Watson Marlow 323 E, Falmouth, UK) at a rate of 30 mL min^{-1}. Appropriate amounts of stock solution of the analytes at 0.3 mL min^{-1} were delivered into the exposure tank using a second peristaltic pump (Minipuls Gilson, Villiers-le-Bel, France). Constant nominal concentrations of 2 or 0.1 μg L^{-1} for each analyte (depending on the experiment) were maintained. Water in the tank was stirred at 40 rpm using an overhead stirrer (RZ1, Heidolph Instruments GmbH & Co. KG, Schwabach, Germany) positioned 10 cm above the samplers. This is important in order to maintain a homogeneous nominal concentration through the tank. Prior to each exposure, the apparatus was operated continuously for a minimum of 48 h without the samplers to allow system stabilization.

A refrigeration unit (Frigedor 3001214, P Selecta, Barcelona) was used to regulate water temperature. A PTFE carousel (custom made at the University of Portsmouth, Portsmouth, UK) was used to simulate an average environmental turbulence and consisted of two horizontal turntables at two levels and a support. All these parts were vertically interconnected by a shaft that was connected to the overhead stirrer (figure 1). Each turntable has a capacity for seven samplers, so each experiment can be performed with up to 14 separate samplers simultaneously. PTFE tubes (i.d. 0.6 mm), Omnifit connectors, and 0.6 and 1.6-mm Tygon tubes were also used for connections.

2.3 *Chemcatcher preparation*

The Chemcatcher bodies that retain both the receiving phase and diffusion membrane were made on PTFE as described previously [19, 22]. An appropriate diffusion membrane was placed on top of the conditioned receiving phase disk (both 47 mm in diameter), avoiding any formation of air bubbles between the two layers. The PTFE body formed a watertight seal against the diffusion membrane and prevented any leakage of external medium into the receiving phase. Once the sampler was assembled, the cavity in front of the diffusion membrane was filled with deionized water and then sealed until use by the PTFE cap and locking ring (figure 2).

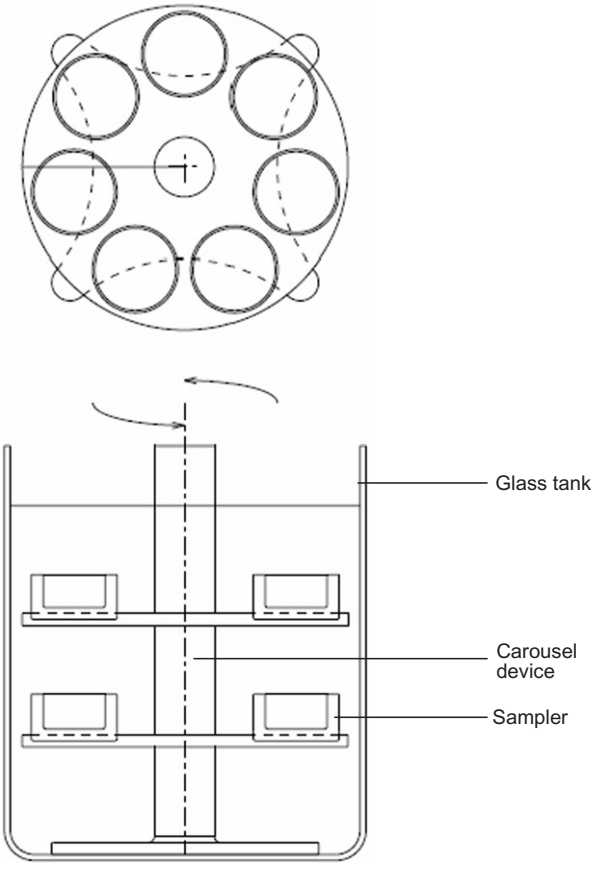

Figure 1. Exposure tank and a carrousel device used in flow-through calibration of passive samplers.

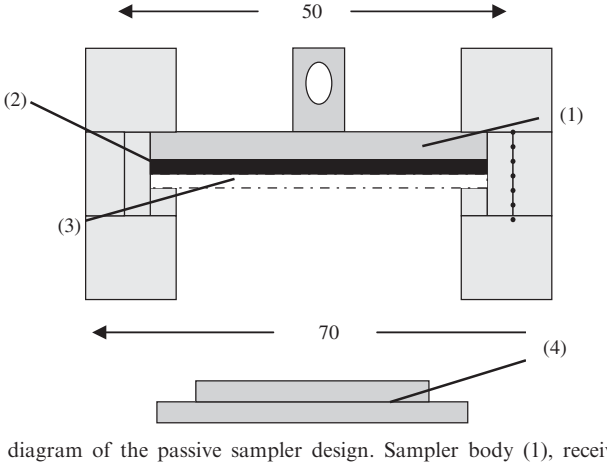

Figure 2. Schematic diagram of the passive sampler design. Sampler body (1), receiving membrane (2), diffusion membrane (3), and screw cap (4).

The receiving disks were conditioned following the manufacturer's recommendations and the cleaning procedures developed throughout our experiments. C_{18}, 47-mm Empore^{TM} disks were conditioned by soaking in a small volume of HPLC-grade methanol for 30 min until translucent. The disks were then rinsed with deionized water to remove the excess of methanol. The SDB-RPS cation-exchange disks were conditioned by washing with acetone (5 mL), followed by methanol (10 mL) and finally by filtering deionized water (15 mL) through the disk to remove all organic solvents. Chelating disks containing iminodiacetic groups (47 mm Empore^{TM}) were first washed with 20 mL of 6 mol L^{-1} of HCl for 30 min in an ultrasonic bath for the removal of traces of mercury contamination. In a vacuum manifold, they were washed with deionized water (50 mL), followed by 3 mol L^{-1} of HCl (20 mL) and then rinsed twice more with deionized water (50-mL aliquots). Finally, 0.1 mol L^{-1} of ammonium acetate buffer at pH 5.3 (50 mL) was added, followed by three washes (20 mL) with Milli-Q water. Disks were stored until use in a Petri dish avoiding drying between conditioning and use.

The diffusion membranes, PTFE sampler body, and tap water used were previously determined to be free of analyte contamination, and a cleaning treatment/conditioning step was not necessary.

2.4 *Extraction of analytes from the receiving phases*

2.4.1 Inorganic mercury. Extractions with two aliquots (10 mL) of concentrated hydrochloric acid (12 mol L^{-1}) were carried out for 10 min in an ultrasonic bath. Recovery was 95–100%.

2.4.2 Organotin compounds (MBT, DBT, TBT, and TPhT). Extraction with one aliquot (8 mL) of acetic acid (13 mol L^{-1}) in methanol for 10 min in an ultrasonic bath. Recoveries for all compounds were in the range of 90–100%, except for MBT, which ranged from 70 to 80%. These recoveries are in the range of those obtained with the optimized extraction procedure used for sediments [23].

2.5 *Derivatization*

Organotins compounds must be derivatized to yield volatile species prior to analysis by GC. A sodium tetraethylborate ethylation procedure similar to that described by Ashby and Craig [24] was used. The whole extract (8 mL) from the receiving phase or 100 mL for water samples was spiked with the TPrT internal standard (final concentration of 70 μg L^{-1} as tin). The derivatization was performed with a mixture of acetic-acetate buffer (2 mL), *n*-hexane (1 mL), and 1% (w/v) $NaBEt_4$ (1 mL). The mixture was mechanically shaken for 10 min, and then the organic layer was transferred to an amber glass vial (4 mL) for subsequent chromatographic analysis.

2.6 *Instrumental analysis*

Inorganic mercury was determined by ICP-MS (HP 4500, Agilent Technologies, Bracknell, UK). Table 1 summarizes the instrumental conditions applied.

Table 1. Instrumental conditions for organotin compounds and inorganic mercury analysis.

	Value
GC parameters	
Injection mode	Splitless (1 min)
Injection volume	1 μL
Injector *T*	250°C
Column	HP-5 (15 m × 0.32 mm × 0.25 μm)
Carrier gas	He, 15 psi
GC programme	50°C (0.5 min) to 250°C (1 min) at 30°C min^{-1}
ICP-MS parameters for organotins	
Transfer line dimensions	80 cm length, 1.5 mm i.d.
Transfer line temperature	250°C
Isotopes	$^{118,119,120}Sn$
RF power	1300 V
Carrier gas	1.2 L min^{-1}
Integration time	0.2 s per m/z
ICP-MS parameters for inorganic mercury	
RF power	1300 W
Carrier gas	1.01 L min^{-1}
Integration time	0.1 s per m/z
Isotopes	$^{200,202}Hg$
Sampling loop	500 μL
Peristaltic pump	11 rpm

Analysis of organotin compounds (MBT, DBT, and TBT) and the internal standard TPrT, after ethylation, was performed by GC-ICP-MS (ICP-MS model HP 4500 and GC model HP 4890, both from Agilent Technologies, Bracknell, UK). The GC was coupled to the ICP-MS through an interface [7] consisting of a PTFE transfer line tube (80 cm long, 1.5 mm i.d.) heated to 250°C. The chromatographic and ICP-MS conditions applied are summarized in table 1.

TPhT cannot be determined directly by GC-ICP-MS due to its high boiling point, which causes its condensation in the interface coupling transfer line. Therefore, GC-FPD (HP 5890 model, Agilent Technologies) with a cut-off filter set at 610 nm (specific for the determination of organotin compounds) was used. Chromatographic conditions were similar to those used in the GC-ICP-MS analysis.

2.7 *Spot water samples from the field*

Spot samples of water from Alicante Harbour (Spain) were collected in glass bottles, and concentrated HNO_3 (1 mL per litre of sampled water) was added for stabilization of inorganic mercury. Organotin compounds were collected in glass bottles and stabilized by adding concentrated acetic acid (1 mL per litre of sampled water). All samples were stored at 4°C until analysis without filtration.

2.8 *Theory of passive sampling*

Different models have been described to explain accumulation patterns in passive samplers [11, 19, 25]. In most of them, a linear uptake is assumed during the initial stage of deployment when back-diffusion of analyte from receiving phase to water is negligible. At this stage, mass accumulated in receiving phase is directly proportional

to deployment time and the aquatic analyte concentration [26] according to the following expression:

$$M_D(t) = M_{(0)} + C_W R_{WD} t \quad (1)$$

where $M_D(t)$ and $M_{(0)}$ are the mass (ng) accumulated in the receiving membrane at a deployment time t (days) and time 0 days, respectively; C_W is the mean water concentration (ng L^{-1}); and R_{WD} is the effective sampling rate (L day^{-1}) which is calculated experimentally under controlled laboratory conditions. The sampling rate is defined as the equivalent volume of water from which the analyte is quantitatively sampled per unit of time.

3. Results and discussion

3.1 *Selection of receiving and diffusion membranes for sampler construction*

The Chemcatcher passive sampler for inorganic mercury, and the Chemcatcher for the organotin compounds MBT, DBT, TBT, and TPhT were made on the basis of three main considerations: (1) the affinity of the receiving phase towards the test substances; (2) permeability of the diffusion membrane for analytes, and (3) an assumption that uptake of analyte was linear with time over typical deployment periods. Different materials were investigated as receiving phases and as diffusion membranes in order to obtain a sampler with optimum performance on the basis of these three considerations.

Among the different receiving disks commercially available, C_{18} was selected for organotins and chelating and cation-exchange SDB-RPS for inorganic mercury. The choice of these disks was based on: (1) the physicochemical properties of the analytes which determine their interaction with the material; (2) previous studies of these receiving phases for other compounds [19, 20], and (3) affinity studies where solutions containing 100 ng (as metal) of test substance were filtered through each candidate disk on which accumulation efficiencies in the range of 90–100% ($n = 5$) were obtained.

To determine the accumulation behaviour of chelating and cation-exchange (SDB-RPS) disks for inorganic mercury and C_{18} disks for organotin compounds, samplers fitted with naked membrane disks were sunk at the bottom of the flow-through tank for 48 h at 11°C and exposed to a 2 μg L^{-1} concentration of analytes. The mass of inorganic mercury accumulated in the cation-exchange disk (SDB-RPS) was approximately 25–30% of that found in the chelating disk. Therefore, chelating material was selected as the receiving phase for inorganic mercury. C_{18} showed good accumulative properties for organotins, so it was selected as the receiving material.

Four different commercially available diffusion membranes, cellulose acetate, dialysis, polyethylene, and polyethersulfone, were assayed for each chosen receiving phase. Three replicates of each sampler configuration were exposed at the bottom of the flow-through exposure tank under the same conditions described above for naked disks (48 h, 11°C, 2 μg L^{-1}).

After exposure, the accumulation factor (AF) was determined as the ratio of mass of analyte accumulated in the receiving phase and its concentration in the water $(M_D(t) - M_{(0)}/C_W)$. Comparison of the different combination of receiving-diffusion disks for each analyte was achieved by their normalized accumulation factors with respect to their corresponding naked receiving disk. Results are given in figure 3.

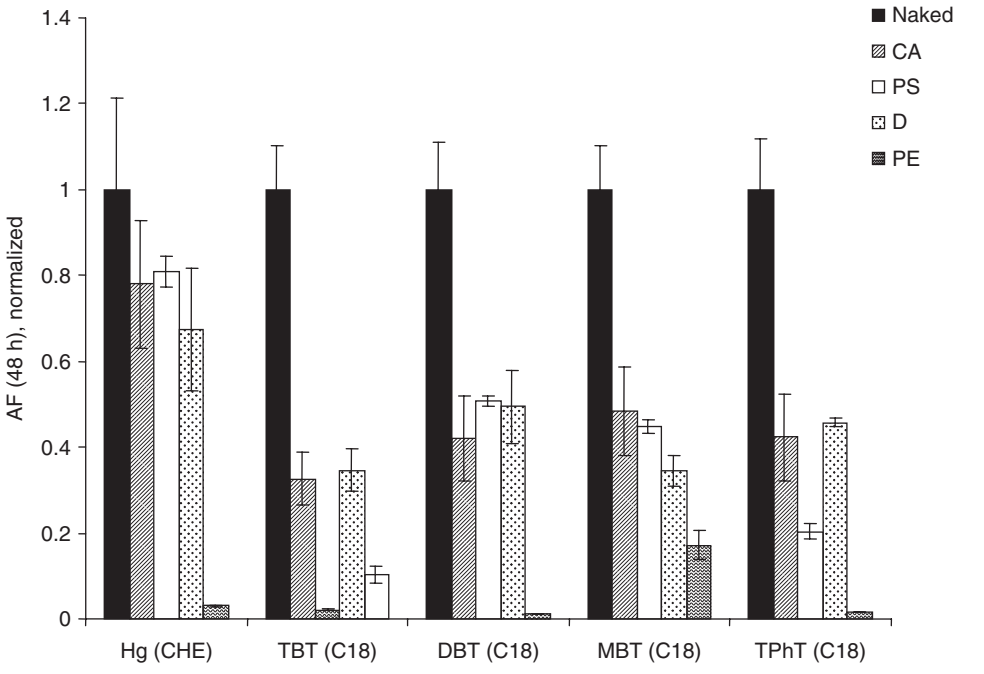

Figure 3. Normalized accumulation factors (AF) (after 48-h exposure) for the different chelating-diffusion membranes (inorganic mercury) and C18-diffusion membranes (organotin compounds) configurations. Key: Naked (receiving phase without limiting membrane), PS (polyethersulphone), CA (cellulose acetate), D (dialysis), PE (polyethylene). Water concentration (C_W) = 2 μg L^{-1}. $n = 3$.

3.1.1 Inorganic mercury. Polyethylene greatly hindered the diffusion of the analyte from water to the receiving membrane. This behaviour was expected on the basis of its hydrophobic nature. However, this material is suitable as a diffusion membrane for neutral Hg species in water, and it is used for this purpose in the PIMS sampler [14].

For cellulose acetate (CA), polyethersulfone (PS), and dialysis (D) membranes, no significative accumulation differences were observed in an one-tailed ANOVA test at the 0.5 confidence level. For these three membranes, the AF decreased about 20–30% with respect to the naked receiving phase. Each of them could be used as diffusion membrane for inorganic mercury. However, the dialysis membrane is prone to biodegradation in the field. Consequently, both chelating disk-Polyethersulfone membrane (CHE-PS) and chelating disk-cellulose acetate membrane (CHE-CA) sampler combinations were further evaluated over longer exposures of 4 and 7 days. The best results in terms of linearity of mass accumulated with time were obtained for chelating-polyethersulfone. Cellulose acetate and polyethersulfone were used for metals and polar organic compounds respectively in the early work of Kingston *et al.* [19] and Persson *et al.* [20].

3.1.2 Organotin compounds. A single sampler design was preferred for all organotin compounds under investigation. As was observed for mercury, polyethylene membrane (PE) hindered the diffusion of most of the analytes from water to the C_{18} receiving membrane. Reduced AFs of TBT and TPhT were observed for polyethersulfone

membrane (PS) sampler, which was found to be caused by the accumulation of those compounds by the membrane material. The dialysis membrane could be used but is not recommended because of its rapid deterioration under field conditions. Therefore, the C_{18}-cellulose acetate sampler performed well enough to be considered a suitable configuration for all the organotin compounds. The decrease in the AF with respect to the naked C18 disk was about 60% for TBT and TPhT, and about 50% for the others.

3.2 *Effects of pH, salinity, and biofouling on uptake rates*

The effects of environmental variables such as pH, salinity, and biofouling on the uptake of test analytes were evaluated for the two optimal selected designs of passive sampling devices.

The effects of water salinity (tap water and artificial seawater) and pH (tap water at pH (6.7–7), 8, and seawater at pH 8) on the uptake of mercury (CHE-PS sampler) and organotins (C_{18}-CA sampler) were evaluated in a flow-through tank experiment for 96 h under the same conditions as those used in section 3.1. The results are shown in figure 4. The AF obtained for the different analytes depending on water conditions have been normalized with respect to the AF obtained in the laboratory tap water without pH modification (pH 6.7–7).

For inorganic mercury, the effect of pH in tap water was more important than salinity. In fact, significant differences between AF were found at the 95% confidence level, and a 20% lower accumulation was obtained with pH. The decrease in the AF at the higher pH could be explained by the tendency of inorganic mercury to form

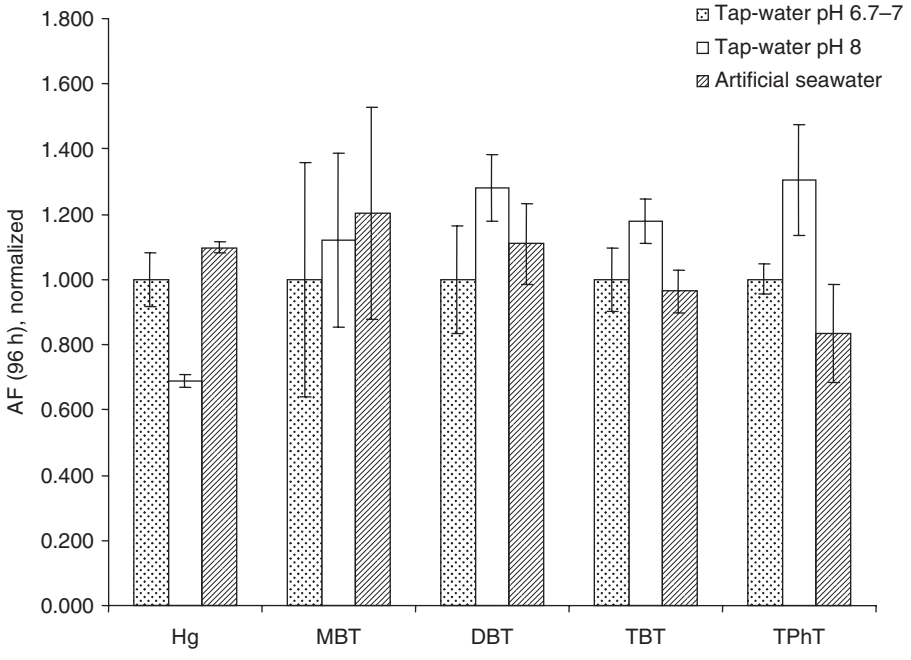

Figure 4. Salinity and pH effects on accumulation factors (AF). AF normalized to AF in tap water at pH 6.7–7; after 96-h exposure. Experimental conditions: 11°C, water concentration (C_W) = 2 µg L^{-1}. $n = 3$.

hydroxylated complexes ($HgOH^+$, $Hg(OH)_2$), which are accumulated to a lesser extent in the chelating receiving phase than the ionic form of the metal. This behaviour would be consistent with the results of earlier work that reported an inverse relationship between pH and mercury bioavailability [27]. For all of the organotin compounds, the AF seems to increase with pH, and no significant differences in accumulation have been observed for a one-tailed Student t test at the 95% confidence level.

When the AFs in artificial seawater (pH 8) are compared with those in tap water (pH 8), no significant effect of salinity at the confidence level of 95% was observed for any of the analytes. These results suggest that the Chemcatcher can be used to monitor all the target compounds in freshwater, estuarine, and coastal marinas, etc.

In order to test the effect of biofouling on sampler performance, the polyethersulfone and cellulose acetate membranes were exposed for 15 days in a natural lake reservoir at a water temperature of 17–18°C and high algal growth. Prior to exposure, the water from the lake was checked for contamination with test analytes. After exposure, a layer of green algae was observed over the surface of the membranes. The fouled and non-fouled membranes were used to construct the correspondent samplers and were exposed for 7 days at the bottom of the flow-through exposure tank, at 18°C and 500 ng L^{-1} of concentration.

Biofouling of the diffusion limiting membrane reduced the uptake of the analytes under study in the range of 10–25%. The greatest effect was observed for the most hydrophobic TBT and TPhT. The biological growth on the diffusion membrane during deployment has been reported as a common problem for most of the developed passive samplers [28]. However, biological growth in these samplers is less severe than for other samplers due to cellulose acetate and polyethersulfone membranes, present a hydrophilic nature [29], and carry a surface negative charge [16], which minimizes biofouling.

3.3 *Time average accumulation and sampling rate (R_{WD})*

To determine the analyte accumulation rate on the receiving disk over an extended time interval, at a controlled temperature and turbulence (reproducing in the laboratory a possible and common environmental condition), 14 samplers of CHE-PS and 14 other samplers of C_{18}-CA, were placed in the rotating carrousel and deployed for up to 14 days in the flow-through calibration tank. The water temperature was fixed at 11°C, and the carousel rotation speed was 40 rpm, equivalent to a linear sampler velocity (ν_s) of 40 cm s^{-1} as has been stated by Vrana *et al.* [21]. The nominal analyte concentration in the tank was 100 ng L^{-1} (as mercury and tin). Two or three replicates of each sampler configuration were retrieved after 2, 5, 8, 11, and 14 days of exposure, and the amounts accumulated in the receiving disk ($M_D(t) - M_{(0)}$) were determined. The sampling rates (R_{WD}) for individual test compounds were calculated by dividing the slope of the linear uptake curve by the nominal aqueous analyte concentration over the deployment period, following equation (1). Table 2 shows the linear regression parameters and the sampling rates values obtained for each compound from the uptake curve.

The correlation coefficients are in the range of those obtained for organic compounds in the Chemcatcher [19, 21] and also for other specific samplers [30]. The compound specific sampling rates obtained for all analytes in the two sampler configurations varied from 0.018 L per day for MBT to 0.137 L per day for DBT. These R_{WD} values

Table 2. Linear regressions of the mass accumulated in samplers between 2 and 14 days of exposure time ($n = 5$) and sampling rate (R_{WD}) factors.[a]

Compound	Slope (ng h^{-1})	Correlation coefficient (r^2)	$R_{WD} \pm$ CV (L day^{-1})
Inorganic mercury	0.697	0.942	0.109 ± 0.012
Monobutyltin	0.048	0.983	0.018 ± 0.001
Dibutyltin	0.539	0.932	0.137 ± 0.010
Tributyltin	0.419	0.960	0.117 ± 0.005
Triphenyltin	0.298	0.947	0.060 ± 0.007

[a]Conditions: 11°C and a stirring level of 40 rpm in a carrousel. Nominal concentrations of analytes in water (C_w) = 100 ng L^{-1} (as metal).

are in the same order of magnitude as those obtained with the Chemcatcher device for other organic compounds, e.g. atrazine and dieldrin, and other membrane configurations with similar polarities [19]. These devices therefore provide an effective linear preconcentration of the analytes. Due to the high capacity of the disks, saturation of the receiving disks was not observed.

3.4 *Method sensitivity*

Significant levels of mercury were found in the chelating receiving disk as received from the manufacturer. A rigorous cleaning procedure (see section 2) was necessary before loading the disks in the samplers. No contamination with mercury was found in any of the diffusion membranes.

The method detection limit (MDL) was expressed as the minimum water concentration (C_W) detectable by the sampler after a typical 14-day sampler exposure. This was calculated by substituting into equation (1) the specific instrumental detection limits for a blank sampler (calculated as three times the standard deviation based on 10 replicates of the blank) in the term mass accumulated ($M_D(t)$), and using the specific compound sampling rate obtained in table 2. The sampler specific MDLs were 1.7 ng L^{-1} for inorganic mercury, and 5.9, 0.7, 1.2, and 2.6 ng L^{-1} for MBT, DBT, TBT, and TPhT, respectively.

The MDL for inorganic mercury is significantly lower than that (0.11 μg L^{-1}) for its direct determination from bottle samples of freshwater using CV-AFS [31]. Thus, using passive sampling, this analyte can be determined at those levels found in natural waters without the need for a further pre-concentration step. For organotin compounds, detection limits are low enough for their determination in slightly contaminated waters (4–80 ng L^{-1}) [32, 33].

3.5 *Field trial*

The passive samplers were deployed in Alicante Harbour (Spain) during October 2005. This site was expected to provide a test site representative of commercial harbours with a history of use of organotin-based antifouling agents. Three samplers for organotins (C_{18}-CA) and three samplers for inorganic mercury (CHE-PS) were deployed at the sampling site.

Table 3. Mean analyte concentrations ($n = 3$) obtained for spot sampling at the beginning and the end of exposure, and mean mass in the receiving disk for inorganic mercury and organotins after 14 d of deployment in the Alicante Harbour (Spain).[a]

Analyte	Mean spot water concentration ($ng\,L^{-1}$), day 0	Mean spot water concentration ($ng\,L^{-1}$), day 14	Mass of analyte in the samplers after 14 days (ng)
Mercury	180 ± 4	260 ± 4	51.6 ± 2.8
Monobutyltin	3.7 ± 0.5	4.3 ± 0.5	7.3 ± 0.1
Dibutyltin	3.8 ± 0.4	7.0 ± 1.7	14.2 ± 1.0
Tributyltin	< D.L.	< D.L.	34.1 ± 0.5
Triphenyltin	< D.L.	< D.L.	nd

[a]D.L. of TBT: $9\,ng\,L^{-1}$. D.L. of TPhT: $14\,ng\,L^{-1}$. nd: not detected

A nylon line was used to suspend the samplers in a vertical orientation at a depth of 30–40 cm below the water surface with the diffusion membrane facing downwards to minimize settlement of silt and colonization of its surface by algae. After 14 days, the samplers were retrieved for analysis. Three replicate spot water samples (1 L) were collected from the deployment site at the beginning (day 0) and the end (day 14) of the trial. The average water temperature over this period was 17°C. Table 3 shows the concentrations of test analytes found in spot samples, and the masses accumulated in the receiving phases of the passive samplers over the deployment period.

The levels of inorganic mercury found in spot samples taken from Alicante Harbour were consistent with those reported by Bravo-Sanchez *et al*. [34] for the northern coast of Spain (129–241 $ng\,L^{-1}$), but were higher than those reported for the open Mediterranean Sea during 2002–2005 (1.6 $ng\,L^{-1}$) [35]. These concentrations measured are below the EPA water quality criteria (maximum allowable value 940 $ng\,L^{-1}$) for mercury in sea water [36].

The levels of organotin compounds found in spot samples from the harbour are similar to those found for moderately contaminated areas. Murai *et al*. [37] reported 8.2, 3.3, and 9.0 $ng\,L^{-1}$ for MBT, DBT, and TBT, respectively, on the Western coast of Japan 11 years after restrictions were introduced on the use of organotin antifouling compounds. In contrast, concentrations of TBT up to 200 $ng\,L^{-1}$ have been found in some harbours along the western Mediterranean [32]. TBT was below the detection limit in spot water samples when samples were taken (days 0 and 14), but it was accumulated in the samplers during the 14 days of deployment. In fact, figure 5(a) shows the chromatogram of organotins obtained from an extract of a spot sample of water collected from Alicante Harbour on day 14 and TBT was not detectable. The same happened for the other two samplers deployed. In contrast the chromatogram in figure 5(b) obtained from passive sampler extracts after 14 days of deployment shows a clear peak corresponding to TBT. The accumulation of TBT in the samplers could be a result of punctual discharges of TBT detected by the sampler which is continuously collecting the analytes contrary to spot samples which just provide a snapshot of water status. Since samplers effectively clear analytes from large volumes of water over an extended period of time, the preconcentration achieved is very high.

At this stage, it is not possible to estimate the average water concentrations through the amount accumulated in the passive sampler. To extrapolate the mass accumulated to the time-averaged water concentration, it is necessary to calibrate the samplers under a wide range of controlled laboratory conditions of temperature and turbulence.

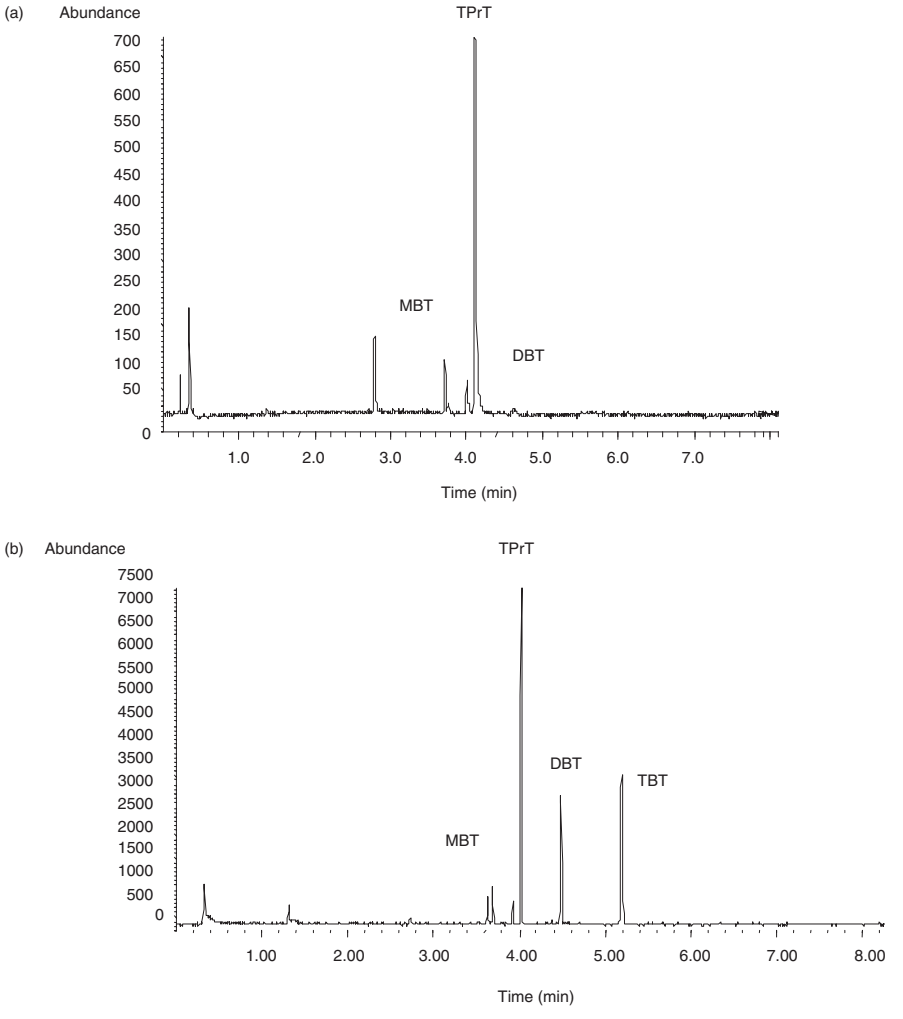

Figure 5. GC-ICPMS chromatograms obtained for organotins (a) spot samples of water taken on day 14 of the trial in Alicante Harbour and (b) passive sampler after 14 days of deployment.

However, it is expected that concentrations estimated by Chemcatcher would be lower than those obtained by spot sampling. Spot samples include also suspended material (in unfiltered samples), and large organic and inorganic colloids in which the analytes could be adsorbed. For the Chemcatcher, the presence of the diffusion barrier in the sampler with a fixed pore size allows the accumulation of only labile fractions of analytes, which are presumed to be bioavailable.

4. Conclusions

The Chemcatcher provides a robust design that is easy to produce, deploy, and prepare for analysis due to the use of a bound solid-phase material as receiving phase.

A Chemcatcher passive sampler configuration was demonstrated for inorganic mercury and other for organotin compounds.

Linear uptake of the analytes was observed for up to 14 days, and a kinetic approach was applicable. Saturation of the receiving phase was not observed for laboratory experiments, and the equilibrium state was not approached during 14 days' exposure at the concentration levels tested. The sampling rates are high enough for these analytes to be useful in environmental monitoring and could offer an alternative tool for the routine monitoring of water quality.

However, further work is necessary to be able to estimate the time-averaged concentrations of the water during the deployment period and to extend the range of calibration data available to cover the range of hydrodynamic conditions and temperature typical of field locations.

Acknowledgements

We acknowledge the financial support of the European Commission, DG Research (contract EVK1-CT-2002-00119; http://www.port.ac.uk/research/stamps/) and the Spanish Science and Education Ministry (CTQ-2004-20349-E) for this work.

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