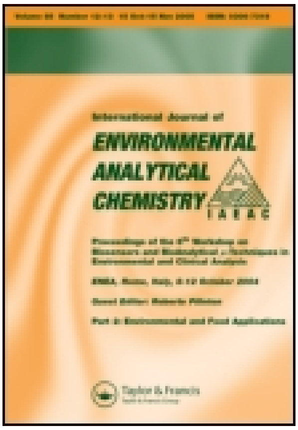

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Mercury and organotin compounds monitoring in fresh and marine waters across Europe by Chemcatcher passive sampler

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Mercury and organotin compounds monitoring in fresh and marine waters across Europe by Chemcatcher passive sampler

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Several field trials have been carried out to assess the performance of the passive sampler Chemcatcher as aquatic monitoring technology for inorganic mercury and the organotin pollutants monobutyltin (MBT), dibutyltin (DBT) and tributyltin (TBT) in different types of waters across ten locations in Europe. Two version of the sampler were used. One for mercury that consists on 47 mm Empore^{TM} disks of iminodiacetic chelating groups as the receiving phase overlaid by a diffusion membrane of polyethersulphone; and other for organotin compounds comprising a C_{18} disk and a cellulose acetate membrane. Both membranes were held in a disposable polycarbonate body. The two samplers were calibrated in the laboratory in a previous work to estimate the pollutant concentration. For field sampling, the samplers were deployed for 14 days. In parallel spot samples were periodically collected during the deployment period for comparison purposes. No significant biofouling on the samplers was observed for the locations monitored. In general, water concentrations estimated by Chemcatcher were lower than those found in spot water samples due to the device only collected the soluble bioavailable fraction of target pollutants. However, the pre-concentration capability of Chemcatcher allowed the determination of the tested pollutants at levels where spot sampling fails, even in difficult water bodies such as sewage treatment plants. These advantages lead to consider this emerging methodology as a complementary tool to traditional spot sampling.

Keywords: passive sampling; Chemcatcher; mercury; organotin compounds; speciation; pollution; water monitoring

1. Introduction

Due to its accumulative properties and toxic effects to aquatic organisms and human health, inorganic mercury and organotin compounds (mainly butyltin) have been included in the list of priority pollutants of European Union and in those regulations of US Environmental Protection Agency (EPA) [1–3]. Their chemical monitoring through Europe will rely on the availability of emerging low-cost technologies, tools and methodologies of sampling. Feasibility, appropriateness and robustness are also important requirements. These methodologies could complement or replace traditional sampling methods.

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Organotin compounds, and particularly tributyltin (TBT), have been widely used since 50s due to their biocide properties. They reach the aquatic environment from the release of antifouling paints in boats, from industrial and urban effluents and from sewage sludge disposal [4]. Their high toxicological effects on aquatic organisms have been well documented [5]. The International Maritime Organization (IMO) established a worldwide ban of TBT in antifouling paints since 1989 [6]. The maximum allowable levels legislated for organotin compounds is 20 $\mathrm{ng\,L^{-1}}$ as tin for total species (WHO) and just 10 $\mathrm{ng\,L^{-1}}$ for TBT in seawater [7]. Meanwhile the European Environmental Quality Standard (EQS) of TBT for all types of waters covered by European Unions Water Framework Directive (WFD) is 0.2 $\mathrm{ng\,L^{-1}}$ [2].

Mercury is known to be a global pollutant between air, water, sediment, soil and organisms. Although anthropogenic emissions have been reduced in the last decades [8], ongoing contamination from mining activity, coal burning, waste incineration, paper and chlor-alkali plants is still a worldwide problem. In aqueous environments, mercury is an important pollutant enhancing its toxicity to organisms by bioaccumulation due to its possible methylation [9]. Consequently measures to control mercury releases have been implemented in Europe and North America. The maximum limit for total mercury content in drinking water is 2 $\mathrm{\mu g\,L^{-1}}$ (USEPA), 1 $\mathrm{\mu g\,L^{-1}}$ (WHO) or the EQS for all types of water covered by WFD which fixed a maximum concentration of 0.05 $\mathrm{\mu g\,L^{-1}}$ for total dissolved mercury [2].

Monitoring studies of organotin compounds [10–14] and mercury [15–17] in aquatic ecosystems carried out rely on collecting samples at specific points and at fixed periods of time. This methodology called spot sampling only offers an instantaneous ‘‘snapshot’’ of water quality at the moment of sampling, and can be misleading where pollutants levels fluctuate. Continuous or repetitive sampling should be necessary to estimate time-weighted average (TWA) water concentrations of the target pollutants, but these techniques imply high costs and are associated with automatic sampling stations, which require a safety location, a power source, and above all, a great volume of water.

Among the robust and low-cost alternatives an emerging methodology for continuous monitoring, is the passive sampling technology [18]. 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 membrane that control the flux rate to the sorptive phase. Until the equilibrium of uptake is not achieved, the mass accumulated in the receiving membrane is proportional to the concentrations of analytes in the sampling media. Among the devices developed for water monitoring, the most applied technique is the Semi Permeable Membrane Device (SPMDs) for hydrophobic pollutants [19]. This technique has been assayed for organotin compounds in a Norwegian fjord and compared to biomonitoring [20]. For metals, the most developed sampler is the Diffusive Gradients in Thin Films (DGT), which has also been applied to mercury monitoring [21]. The Passive Integrative Mercury Sampler (PIMS) has been applied to the elemental mercury monitoring in water or air [22]. Recently several reviews dealing about the state of art on passive sampling have been published [18,23].

In the last years European research groups have worked for the consolidation of the passive sampler Chemcatcher. This device uses commercial solid receiving and diffusion limiting membranes. The dissolved analytes can pass through the diffusion membrane reaching the receiving disk meanwhile particulates, microorganisms and macromolecules with a greater size can not permeate. The combination of different receiving and diffusion phases has allowed the development of various configurations of the Chemcatcher to monitor a wide range of chemicals such as polar and non-polar organic pesticides [24], metals (Cd, Cu, Zn and Pb) [25], inorganic mercury [26] and the organotin compounds tributyltin (TBT), dibutyltin (DBT), monobutyltin (MBT) and triphenyltin (TPhT) [27]. For inorganic mercury an iminodiacetic chelating Empore™ receiving phase and polyethersulphone as diffusion membrane were used. For the organotin compounds, a C_{18} Empore and a cellulose acetate as receiving and diffusion membrane, respectively were used. Both samplers have been calibrated in laboratory tank experiments in order to afford quantitative approach of analytes [26,27].

In this study, the performance of the proposed versions of Chemcatcher has been tested for inorganic mercury, and organotin compounds at different aquatic environments (river, lake and sea water) across Europe. The data obtained have been compared with those obtained by traditional spot sampling.

2. Experimental

2.1 *Chemicals and materials*

All reagents were of analytical grade or better purity. Ultrapure Milli-Q water (Millipore, Ohio, USA) was used to prepare all test solutions. Standard stock solutions ($1000\,\mathrm{mg\,L^{-1}}$) of inorganic mercury chloride, the organotin chloride compounds MBT, DBT, TBT, 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, Spain) 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 $0.24\,\mathrm{mol\,L^{-1}}$ distilled hydrochloric acid (37% w/v, Scharlab, Barcelona, Spain) 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 derivatising agent of the organotin compounds in a $2\,\mathrm{mol\,L^{-1}}$ acetic-acetate buffer ($\mathrm{pH} = 4.6$). 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, Spain) and Milli-Q water to give the final volume.

Receiving phases of C_{18} and iminodiacetic chelating (CHE) disks (Empore™, 47 mm diameter) were obtained from 3 M (Bioanalytical Europe, Neuss, Germany). The C_{18} disks were conditioned by soaking in a small volume of HPLC grade methanol for 30 min until translucent. The disks were then rinsed with deionised water to remove the excess of methanol. No contamination by the test analyte was found in the receiving phase. The chelating disks (with a complexation capacity of 45 mmoles divalent metals) were first washed with 20 mL of $6\,\mathrm{mol\,L^{-1}}$ HCl for 30 min. in an ultrasonic bath for the removal of mercury contamination. For pre-conditioning, the disk was washed with deionised water (50 mL), followed by $3\,\mathrm{mol\,L^{-1}}$ HCl (20 mL) and then rinsed with water ($50\,\mathrm{mL} \times 2$). Finally, $0.1\,\mathrm{mol\,L^{-1}}$ ammonium acetate buffer at pH 5.3 (50 mL) was added, followed by washes with water ($20\,\mathrm{mL} \times 3$). Receiving disks were stored in a Petri dish and kept damp until use.

Diffusion membrane materials of polyethersulphone (PS) (Z-Bind™ 0.2 µm pore size) and cellulose acetate (CA) (0.45 µm pore size) were purchased from Pall Europe

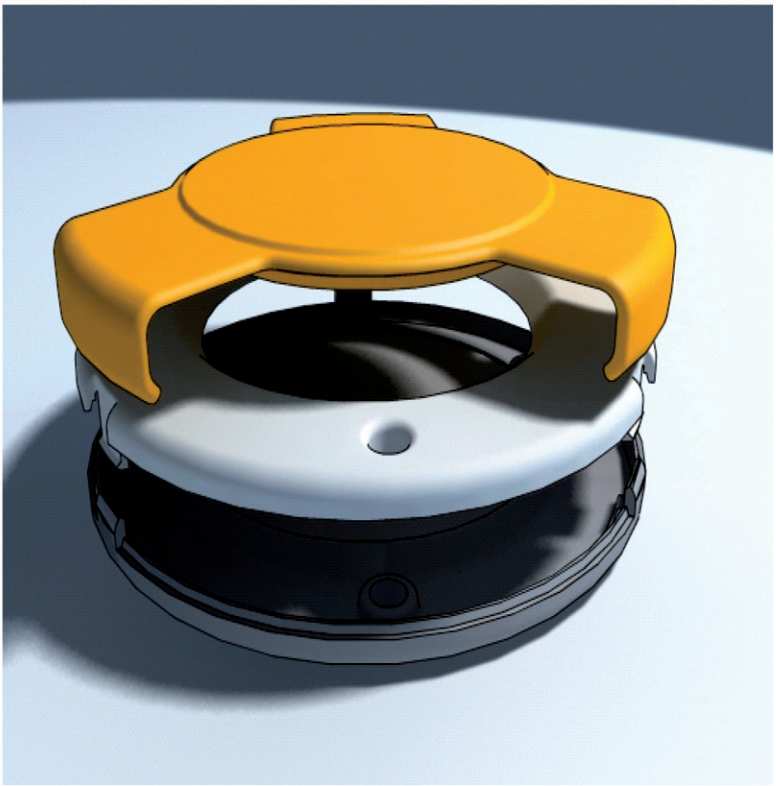


Figure 1. Chemcatcher passive sampler design. The receiving phase and diffusion membrane are housed between the bottom and top sections, which are pressed together to achieve a watertight seal.

(Portsmouth, UK). These membranes were free of contamination and did not require a preconditioning step before use.

2.2 *Chemcatcher preparation, deployment and extraction*

The sampler is a disposable device for a single field deployment that consists of three pieces made of extruded polycarbonate (PC) which are clipped together; two body parts of 70 mm each that fit together retaining both the receiving phase and diffusion membrane inside and a lid for storage and transport. The active surface area of the device is 17.5 cm^2. Figure 1 shows the configuration of the Chemcatcher. When inorganic mercury and organotin compounds were monitored, 8 samplers for each configuration and for each place were shipped refrigerated, closed by a transportation lid and enclosed separately in a polyethylene zip-lock bag. At each sampling point 6 samplers were deployed for 14 days 0.5–1 m below water surface attached to a stainless steel bar with a nylon rope (Figure 2). The remaining 2 were used as field blanks.

Three extra samplers were prepared as laboratory blanks for each version of the device. These samplers were maintained at the laboratory refrigerated at 4°C during the whole trial.

Figure 2. Arrangement of Chemcatcher samplers for deployment.

After deployment, the samplers were filled with water from the sampling site, sealed with the sampler cap and transported refrigerated to the laboratory.

The procedures for the extraction of the analytes contained in the receiving disks were the following:

Inorganic mercury: Extraction with two aliquots (10 mL) of concentrated hydrochloric acid for 10 min. in an ultrasonic bath. Recovery was 95–100%.

Organotin compounds (MBT, DBT and TBT): 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 90–100% except for MBT which ranged from 70–80%.

Figure 3 shows the whole passive sampling protocol for the field trial study.

2.3 *Description of studied locations*

The field trials have been conducted from 2005 to 2006 at different sites in Europe including an estuary, two rivers, a lake and two harbours.

Table 1 shows for the analytes sampled, the sampling locations and a brief description of the site. Some features of each site are the following:

Alicante harbour (Spain): Located at the East of the Mediterranean Sea. The samplers were deployed inside the docks where water pollution, mostly by organotin compounds but also by inorganic mercury, was supposed to be higher due to ship activity.

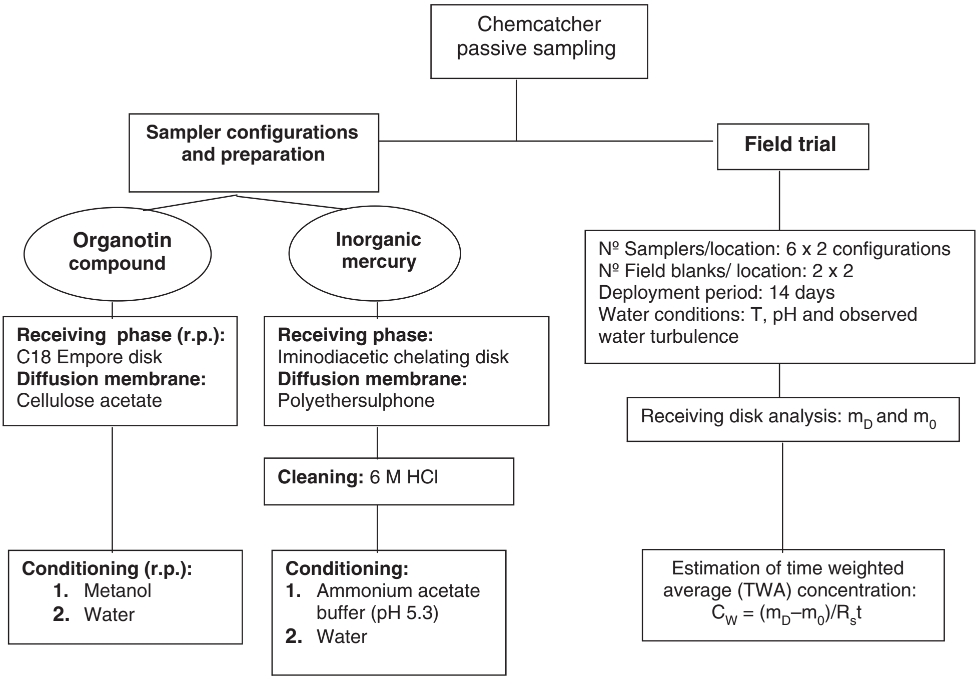


Figure 3. Diagram presenting the passive sampling protocol.

Portsmouth Naval Base (UK): This harbour was located in the Atlantic Sea at the South of the UK. The passive samplers were deployed outside the docks so it was affected by tides, and inside.

Velsen water treatment plant (The Netherlands): This plant was located in the course of the Meuse River. The Meuse River presents a total length of 925 km. It runs across north eastern France, southern Belgium and the Netherlands.

San Juan Reservoir (Spain): It is located at the southwest of Madrid ant it is feed with water from the Cofio and Alberche rivers. It has a surface of 650 ha and a capacity of 138 hm^3. These features have favoured its use for irrigation, recreational boating and fishing activities.

Cinca River (Spain): This River is a tributary of the Ebro River (Norteast of Spain). The sampling point was located in a heavy industrialised town and presents an important chemical industry.

Valdeazogues River (Spain): This River runs east–west along the Almadén area with an important mercury mining activity in the past, which was suspended in the year 2000. Two sampling locations were chosen up- and downstream of the main extraction mines respectively.

Ribble Estuary (UK): This estuary is located in the west coast of UK in the Irish Sea; it presents a length of 18 km and an acute effect of tides, which favoured the mixture of fresh and seawater. Two sites have been selected for monitoring between the estuary and the town of Preston, one in the proximity of the docks and the second one in the docks.

Table 1. Sampling locations.

Location	Deployment period	Site description (GPS coordinates)	Analytes
Alicante Harbour (Spain)	November 2005	Commercial harbour (38.335277, −0.489385)	Mercury Organotins
Portsmouth Harbour (UK)	September–October 2005	Naval base. Site 1. Outside the docks (50.809731, −1.107645) Site 2. Inside the docks (50.808620, −1.100864)	Organotins
Velsen (The Netherlands)	October 2005	Sewage treatment plant (52.466024, 4.635437)	Organotins
San Juan Lake (Spain)	May 2005	Sporting boats activity (40.384834, −4.345522)	Mercury Organotins
Cinca River (Spain)	November–December 2005	Chemical plants activity (41.917759, 0.176039)	Mercury
Valdeazogues River (Spain)	February–March 2006	Almadén area with a cinnabar mine Site 1 Los Carrizos (38.736143, −4.810982) Site 2 P. de Hierro (38.72543, −4.870033)	Mercury
Ribble Estuary of Preston (UK)	October 2005	Site 1. Outside the docks (53.728582, −2.940731) Site 2. Inside the docks (53.76027, −2.741303)	Mercury Organotins

2.4 *Spot samples collection from the field*

Spot samples of water were collected with a frequency depending on facilities: every three days or at the beginning and the end of the passive samplers' deployment. Water intake was performed at about 80–100 cm below surface. Water temperature and pH were monitored.

Samples were collected in glass bottles and for the stabilisation of inorganic mercury, concentrated HNO_3 (1 mL per L of water sampled) was added. Organotin compounds were stabilised by addition of concentrated acetic acid (1 mL per L of sampled water). All samples were stored at 4°C until analysis without filtration.

2.5 *Chemical analysis*

2.5.1 *Derivatisation procedure for organotin compounds*

Organotins compounds have to be derivatised to yield volatile species prior to analysis by gas chromatography (GC). A sodium tetraethylborate ethylation procedure was used. The whole extract (8 mL) from the receiving phase of the sampler or 100 mL from water samples were spiked with TPrT internal standard (final concentration of 70 $\mu g\,L^{-1}$ as tin). The derivatisation was performed with a mixture of acetic-acetate buffer (2 mL), 1% (w/v) $NaBEt_4$ (1 mL) and *n*-hexane (1 mL) for extraction of the derivatised analytes. 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.

2.5.2 *Apparatus and instrumental analysis by flow injection-inductively coupled plasma spectrometry (FI-ICP-MS) and GC-ICP-MS*

Inorganic mercury was determined by FI-ICP-MS (HP 4500, Agilent Technologies, Bracknell, UK) equipped with a Babington type nebuliser, a Fassel torch and a double-pass Scott-type spray chamber cooled by a Peltier system. The ICP-MS was operated at a power of 1300 W with a carrier gas flow of 1.01 $L\,min^{-1}$. The sampling loop was 500 µL. Data were collected by monitoring specific mercury ions at $m/z = 200$ and $m/z = 202$ with a 0.1 s integration time per isotope.

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 consisting on a PTFE transfer line tube (80 cm long, 1.5 mm i.d.) heated to 250°C [31]. The GC was fitted with a non-polar fused silica capillary column HP-5 (cross-linked 5% phenylmethylsilicone, 15 m long × 0.32 mm i.d., with a 0.25 µm film thickness, Agilent Technologies, Spain) and operated under the following conditions: splitless injection mode; injection port temperature 250°C; injection volume 1 µL; oven temperature programme: 50°C (0.5 min) then 30°C min^{-1} to 250°C (1 min). The ICP-MS was operated at a power (RF) of 1350 W with a carrier gas flow-rate of 1.2 $L\,min^{-1}$. Data were collected by monitoring ions (0.2 s integration time per isotope) at $m/z = 118$, 119 and 120 specific for the tin. The ICP-MS was tuned using ion $m/z = 126$, corresponding to the xenon present in the argon plasma gas.

2.6 *Estimation of passive sampler TWA concentrations: kinetic theory of the sampler*

Reviews of the principles governing the uptake of an analyte by different designs of passive sampling devices constructed from a receiving phase and a diffusion membrane, including the Chemcatcher, have been published [21–27]. Briefly, the uptake of a chemical into a sampler can be divided into three stages: linear, curvilinear and finally equilibrium state. During initial deployment accumulation is approximately linear. At this stage, the mass of analyte in the receiving phase is directly proportional to the concentration to which the system has been exposed, the deployment time and the effective sampling rate (R_s) following the equation:

$$m_D = m_0 + C_W R_s t, \tag{1}$$

where m_D = mass (ng) of target analyte accumulated in the receiving phase, m_0 = initial mass (ng) of the analyte in the receiving phase, C_W = the analyte concentration in water (ng L^{-1}), R_s = effective sampling rate of the device (L day^{-1}) and t = deployment time (days).

R_s represents the equivalent volume of water cleared of analyte per unit of time and is analyte specific, but its value is also depending on the environmental conditions, mainly temperature and turbulence. R_s has been determined experimentally at the laboratory using a flow-through calibration tank at a fixed concentration of analyte (C_W) and at different temperature and turbulence to reproduce possible environmental conditions. The uptake curve (Equation 1), is obtained as the amount of analyte accumulated in the receiving phase *versus* the sampler exposure time. The slope of the calibration curve is C_wR_s and therefore, R_s can be calculated at each experimental condition. In previous works [26,27], the effects of temperature and turbulence on the performance of the CHE-PS Chemcatcher for the sampling of mercury and the C_{18}-CA Chemcatcher for organotin compounds were studied. Samplers were deployed in the calibration tank for up to 14 days at three water temperatures (4, 11 and 18°C), three levels of turbulence ($0, 40, 70\,\text{cm s}^{-1}$ of linear velocity of the water) and at a constant concentration (C_w) of analyte (0.2 or $0.4\,\mu\text{g L}^{-1}$). After exposure, the amount of analyte (m_D) accumulated in the receiving phase was measured. Satisfactory linear regression for most conditions tested was observed over a deployment period of 14 days at a relatively high concentration used in the tank. This provides evidence that the sampler is operating in a region far from equilibrium.

Table 2 shows the *R*s values obtained at each experimental condition. These values, should allow a reasonable estimation of TWA concentrations in flowing field waters. By the application of the calculated *R*s values, the TWA concentrations for each sampling location were calculated according to the expression:

$$\text{TWA} = \frac{m_D - m_0}{R_s t}. \tag{2}$$

2.7 *Quality control and method quantification limits*

The application of appropriate quality control (QC) procedures is mandatory for the use of any passive sampler. Appropriate QC samples should be prepared to quantify background levels in the receiving phase, and possible contamination during transport, deployment, retrieval, storage, processing and analysis. Apart from the commonly used reagent and procedural blanks, two different types of QC Chemcatchers are used: fabrication blanks and field blanks. Fabrication blanks are prepared in parallel to samplers for deployment and are kept refrigerated and filled with deionised water in the laboratory during the sampling campaign. Field blanks are samplers that account for

Table 2. Chemcatcher sampling rates (R_s) for mercury and organotin compounds in the flow-through tank calibration experiments at different water temperatures and levels of simulated water turbulence. Results are expressed as mean $R_s \pm$ coefficient of variation ($n = 3$).

Compound	Stirring level (degree of water turbulence)	Sampling rate, mL day^{-1} (water temperature)		
		Rs (4°C)	Rs (11°C)	Rs (18°C)
TBT	SL 1	*	29 ± 12	56 ± 17
	SL 2	42 ± 11	117 ± 27	106 ± 25
	SL 3	174 ± 36	201 ± 21	202 ± 28
DBT	SL 1	*	41 ± 25	48 ± 14
	SL 2	45 ± 8	137 ± 34	141 ± 36
	SL 3	129 ± 22	189 ± 32	204 ± 28
MBT	SL 1	*	6 ± 2	4 ± 1
	SL 2	3 ± 1	18 ± 5	11 ± 3
	SL 3	23 ± 7	22 ± 5	18 ± 7
Mercury	SL 1	*	29 ± 9	31 ± 11
	SL 2	80 ± 18	84 ± 19	87 ± 22
	SL 3	70 ± 16	91 ± 20	94 ± 26

Notes: TBT: Tributyltin, DBT: Dibutyltin, MBT: Monobutyltin.
SL1: samplers deployed at the bottom of the calibration tank.
SL2: Samplers rotating at 40 rpm.
SL3: Samplers rotating at 70 rpm.
*Due to the long lag-phase under these conditions the sampling rate was not measured.

contamination during transport to and from each sampling location. These are transported under the same conditions as deployed samplers and are exposed to ambient air during both deployment and retrieval. During the whole sampling period these are kept refrigerated and filled with deionised water.

Another factor to be considered is the number of samplers deployed, and the number of blanks to be used at each field location. The number of samplers used will depend on the required confidence level for the data obtained. It is generally recommended that 2–3 field and laboratory blanks and 4–6 exposure Chemcatcher samplers be used at each location. The difference in concentration between replicates was usually less than 10% for QC blanks and about 20% for exposure samplers.

The quantification limit depends on the sampling rate, the exposure period and the detection limit of the analytical technique. The overall method detection limits (MDL), were calculated as the minimum aqueous concentration (C_w) of Hg and organotin compounds detectable by the sampler after a typical 14 days field exposure. This was calculated by substituting into Equation (2) the FI-ICP-MS and GC-ICP-MS instrumental detection limits for Hg and for organotin compounds, respectively, for a blank sampler (calculated as 3 times the standard deviation based on 10 replicates) in the mass accumulated (m_D) term. The MDL ranged between 2.2 and 2.9 ng L^{-1} for Hg and 0.2 and 2.0 ng L^{-1} (as tin) for the organotin compounds at the water temperatures of 11 and 18°C and at medium (40 cm s^{-1}) and high (70 cm s^{-1}) water turbulences. The method quantification limit (MQL) ranged between 7.3 and 9.7 ng L^{-1} for Hg and 0.7 and 7.0 ng L^{-1} for the organotin compounds. These concentrations are low enough to enable monitoring levels of mercury and organotin analytes by the developed passive sampler in most contaminated aquatic environments.

3. Results and discussion

3.1 *Appearance of the passive sampler after deployment*

The biological growth on the diffusion membrane during deployment has been reported as a problem for most of the developed passive samplers [28]. Biofouling increases the thickness of diffusion membranes reducing their permeability to target analyte which yields to an underestimation of TWA concentration. In the present study no significant biological growth was observed in those samplers exposed to marine water, meanwhile a slight biofouling was observed for those exposed to fresh water, mostly in those samplers exposed in the sewage treatment plant. The diffusion membranes employed, cellulose acetate and polyethersulphone, present a hydrophilic nature and carry a surface negative charge [29], which minimise biofouling. Furthermore, the streamlined body of the Chemcatcher reduced effectively the risk of covering the active surface. However, a small silt deposition in all the exposed samplers was observed, although they were exposed facing downwards. The polycarbonate body proved to be robust against mechanical damage and no leaching interfering compounds from the body to the receiving phase was observed along field trial.

3.2 *Spot water concentration and accumulation and estimation of TWA concentration by passive sampling*

3.2.1 *Spot water for organotin compounds*

Table 3 shows the concentration found for organotin compounds by spot and Chemcatcher sampling. The levels of organotin compounds found in spot samples were in agreement with those found for moderately contaminated areas [10–14]. Even TBT concentrations up to $200\,\mathrm{ng\,L^{-1}}$ have been found in some harbours along the western Mediterranean [30]. For Portsmouth harbour and Ribble estuary, differences between the levels measured at the two sampling sites showed the location dependency in organotin aquatic levels. In both cases, site 1 was located outside the docks and it was more affected by tides than site 2, which was inside the docks. The higher concentrations found at site 2 confirmed the source of TBT as additive in antifouling paints and the presence of DBT and MBT mainly as degradation products of this compound. The same explanation could be applied to Alicante harbour where sampling point was located inside the docks. The Butyltin Degradation Index (BDI), which is useful to predict if the organotin contamination is recent or not, is given by the ratio between MBT and DBT concentrations over the TBT level [31].

$$\mathrm{BDI} = \frac{[\mathrm{MBT}] + [\mathrm{DBT}]}{[\mathrm{TBT}]}. \tag{3}$$

For Alicante harbour BDI was $1.4\,\mathrm{ng\,L^{-1}}$, for Portsmouth (site 2) $3.5\,\mathrm{ng\,L^{-1}}$ and for Ribble estuary (site 2) $5.2\,\mathrm{ng\,L^{-1}}$. In all cases BDI values implied a moderately, for the first, and more relevant for the others, degradation of TBT towards the other organotin compounds without recent inputs of TBT.

Table 3. Results of field study by spot and Chemcatcher passive sampling for organotin compounds.

	MBT		DBT		TBT	
Location	Spot (ng L^{-1})	TWAC (ng L^{-1})	Spot (ng L^{-1})	TWAC (ng L^{-1})	Spot (ng L^{-1})	TWAC (ng L^{-1})
Alicante Harbour	12.1 ± 5.4	8.7 ± 4.4	27.3 ± 7.6	4.6 ± 1.3	12.3 ± 4.5	8.2 ± 2.2
Porstmouth Harbour, site 1	7.9 ± 4.2	6.1 ± 1.5	<dl	1.7 ± 0.6	<dl	4.7 ± 1.8
Porstmouth Harbour, site 2	12.7 ± 4.5	7.8 ± 0.8	30.0 ± 12.0	2.3 ± 0.4	6.23 ± 1.2	4.2 ± 0.7
Velsen Plant	13.8 ± 2.5	13.0 ± 4.0	<dl	2.6 ± 0.9	<dl	4.7 ± 1.8
S. Juan Reservoir	4.0 ± 2.0	9.1 ± 0.5	9.0 ± 5.0	2.6 ± 0.3	<dl	<dl
Ribble Estuary, site 1	4.6 ± 0.5	<dl	<dl	2.1 ± 0.1	<dl	4.4 ± 0.3
Ribble Estuary, site 2	13.5 ± 7.0	6.0 ± 1.4	33.6 ± 10.4	4.8 ± 0.4	9.1 ± 1.9	6.4 0.8

Notes: TWAC: Time Weighted Average Concentration.
Rs value applied: 18°C SL2 (Alicante harbour and S. Juan reservoir) and 11°C SL2 (Portmouth harbour, Velsent plant and Ribble estuary).
dl Detection limits in spot samples: MBT = 2 ng L^{-1}, DBT = 5 ng L^{-1},TBT = 9 ng L^{-1}.
Chemcatcher detection limits (dl): MBT = 3.4 ng L^{-1}, DBT = 0.7 ng $L^{-1}$and TBT = 1.2 ng L^{-1}.

Before restrictions on TBT usage in antifouling paints (year 1989) monitoring programs carried out in European marinas showed levels higher than $500\,\mathrm{ng\,L^{-1}}$. Recent studies have reported a general decline of TBT in aquatic ecosystems with concentration values rarely exceeding $100\,\mathrm{ng\,L^{-1}}$ [32].

For wastewater from the Velsen water treatment plant (N.D.), MBT level was significant. The other species were not detected. Degradation towards the less butylated compound could be possible during the wasterwater treatment.

As it was expected, the organotin levels found in the San Juan reservoir (Spain) for freshwater were lower than those found for seawater. Although this location is a marina where the long residence times of small boats could lead to a continuous lixiviation of paint additives, the absence of TBT and the low level of DBT and MBT seem to be the result of an efficient application of the regulations for the removal TBT from antifouling paints.

3.2.2 *Chemcatcher sampler for organotin compounds*

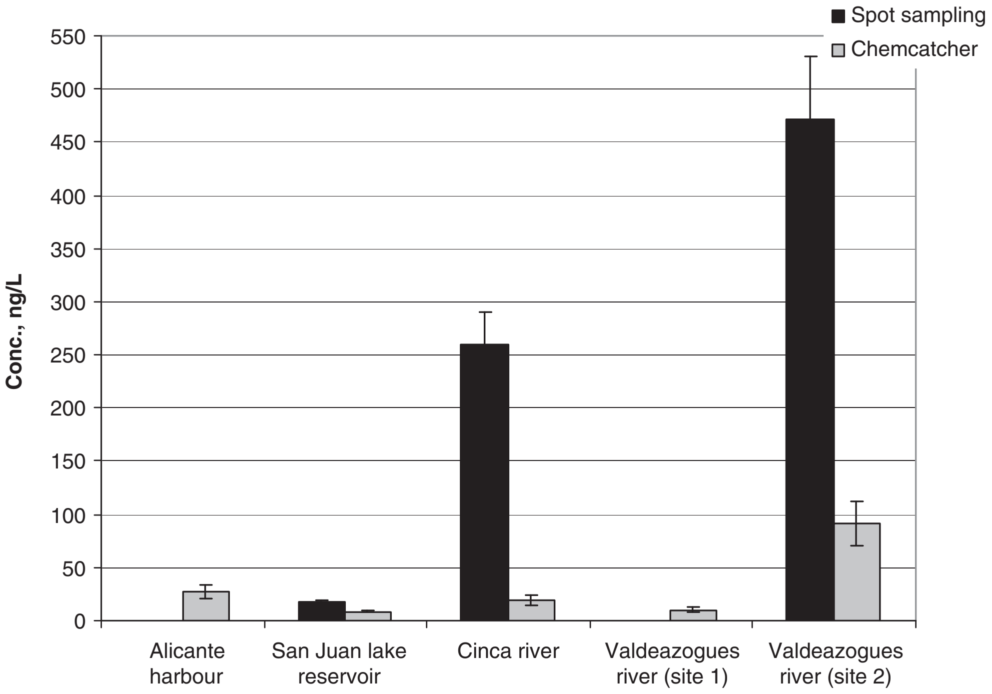
Table 3 shows the estimated TWA concentration for the organotin compounds by passive sampling at the different locations, calculated from Equation (2) and the mean mass accumulated in the receiving phase of the six samplers after 14 days of deployment. This device presented good accumulation and reproducibility properties after 14 days of deployment, which allowed overcoming instrumental detection limits improving its sensitivity. The R_S chosen was the closest to water characteristics in terms of temperature and turbulence. The lack of a system to measure the turbulence during the field trials led to consider a medium turbulence for all by the observations performed at each sampling points. Regarding TWA concentrations estimated by Chemcatcatcher, it is important to highlight the capability of the sampler for sequestering and consequently estimate all organotin species in those locations where spot sampling allows the determination of just one or two compounds.

TWA concentration for TBT and DBT differed up to one magnitude order with those given by spot sampling, as can be also observed Table 3. This fact is common for most passive sampler devices and it is attributed to the differences in the polluted water fractions measured by spot and passive sampling methodologies. Water concentration estimated by passive samplers corresponds to the dissolved bioavailable fraction and it does not account for the pollutant bound to particles and colloids in water. DBT and TBT physicochemical properties favour their sorption to dissolved organic material and suspended particulate matter that could be contained in the spot water. Nevertheless, the TWA concentrations for MBT were close to the concentration obtained by spot sampling for most of the sampling sites. This could be due to a lower trend on MBT association to particulate matter [13,32].

Sample filtration was not recommended due to the risk of analyte loss and this provided a more marked difference between the levels given by the two sampling methodologies.

3.2.3 *Spot for mercury*

Figure 4 shows the concentration of inorganic mercury in the spot water samples for the places monitored. Important levels have been found in the Cinca (Spain) and the Valdeazogues (Spain) Rivers due to the industrial and mining activities respectively.



Rs value applied: 84 ± 19 mL d^{-1}

Spot sampling concentration in Alicante harbour and Valdeazogues river (site 1) < Detection limit (14.2 ng L^{-1})

Chemcatcher Detection Limits (dl) = 1.7 ng L^{-1}

Figure 4. Mean concentration of inorganic mercury determined by both spot and passive sampling at the different locations assayed. Passive sampling bars show the concentration estimated from the average masses recovered in 4–6 replicates samplers. Spot sampling bars show the average concentration of those samples regularly taken.

In the Cinca River, mercury measured concentration exceed that estimated at the same sampling location, the town of Monzón, in the period 2002–2005 whose levels were in the range 100–50 ng L^{-1} [33]. Moreover, it is important to highlight a continuous input of mercury in this river with probably temporal variation due to peaks in industrial activity, so a continuous mercury monitoring is recommended to obtain a real picture of water status.

In the case of Valdeazogues River contaminated by the Almadén cinnabar mine, mercury levels are consistent with those measured for the 1995–1997 period (dl −620 ng L^{-1}), where an important spatial and temporary variation in mercury concentration was reported [16]. This variability also appears in this study, as can be observed for the values obtained for the two sampling points and by the value of standard deviation given for the average water concentration at the site 2. Mercury levels in surface waters reported for other abandoned mercury mining areas in Asturias (North of Spain) ranged between 0.5–90.8 μg L^{-1} and 10^{-3}–2.5 μg L^{-1} [17].

The levels found are higher than those reported for mercury at other European polluted and non polluted rivers, such as the polluted Pigüeña river in the north of Spain whose levels were in the range 120–130 ng L^{-1} [15] or those reported for the Gironde estuary (France) in which mercury levels ranged between 0.74 and 2.94 ng L^{-1} [34], and even to those given for the Lot-Garone River (France) (0.6–1.5 ng L^{-1}) which was historically mercury polluted by a coal mining and zinc ore treatment [9].

3.2.4 *Chemcatcher sampler for inorganic mercury*

Figure 4 shows the estimated TWA concentration for inorganic mercury by passive sampling after 14 days of deployment at the different locations and a comparison with mean water concentration found by spot and sampling. At all locations, except the Alicante harbour, there is a great difference respect to spot sampling values. An alkaline nature has been reported for both rivers [16,33] which reduces mercury bioavailability [35]. For Cinca River, 20 mg L^{-1} of suspended matter has been reported for the sampling period, which favours mercury sorption, minimising its bioavailability. In San Juan Reservoir suspended matter and organic content is higher than in rivers, mainly in spring when the sampling period was performed. For all sampling locations, the percentage of dissolved mercury respect total content given by spot sampling ranged about 20% which is in agreement with the percentages reported at different locations at the Lot-Garone River Basin (France), in which dissolved mercury levels ranged between 7 and 53% [9].

Other reason to explain the differences found between measured levels by spot and passive sampling is the fluctuation of target analytes during sampler deployment [24]. For inorganic mercury, spot water concentration varied between 883 ng L^{-1} at the beginning and 60 ng L^{-1} at day 14 of the trial performed at the Valdeazogues River (site 2). Therefore, only daily spot sampling could detect any change in aqueous concentration during these intervals. Inorganic mercury in surface oxic waters is not present as free ion, it trends to be bound to variable amounts of hydroxide and chloride depending on pH and chloride levels. Also in seawater it is bound to sulphides. Another fraction is bound to humic acids and dissolved organic material. It has been reported that nearly 95% of inorganic oxidised mercury in lakes is bound to dissolve organic matter [36].

4. Conclusions

This work has demonstrated the effectiveness and feasibility of the passive sampler Chemcatcher to monitor the dissolved fraction of inorganic mercury and the organotin compounds TBT, DBT and MBT in different type of waters using a simple and low cost deployment system.

As it was observed, in most sites the sampler provides an estimation of TWA concentration for most of the target compounds, even in the case than their levels are below detection limits for traditional spot water sampling. The sampler shows a good *in situ* pre-concentration capacity for at least 14 days of deployment, this overcomes the sensitivity and stability problems found in the determination of these pollutants at the natural levels. This passive sampler presents a good reproducibility in mass accumulation, even at the low and fluctuating levels of these pollutants in flowing waters.

Chemcatcher sampler seems to be a good tool for the aquatic monitoring of target analytes.

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