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Seawater quality control of microcontaminants in fish farm cage systems: Application of passive sampling devices

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ABSTRACT

Increasingly, developed countries are imposing restrictions on chemicals used in aquaculture, and introducing residue monitoring programmes to ensure the highest possible seafood safety standards. Chemotherapeutants, additives or chemical residues in edible tissues of aquaculture products are now attracting attention, and a major issue is the accumulation of microcontaminants in seafood flesh. Environmental quality control is related to the provision of high-quality, safe products. The present paper evaluates the effectiveness of passive sampling devices as tools in environmental monitoring programmes for fish farm cage systems. Capability to detect trace levels of microcontaminants, sampling rates, and accumulation kinetic is assessed. Devices tested were Polar Organic Chemical Integrative Samplers (POCIS), for detecting pharmaceuticals, pesticides and hormone residues; Semi-Permeable Membrane Devices (SPMD), to detect bioaccumulable pollutants; and Diffusive Gradients in Thin films (DGT), for metals.

Keywords: Fish farm cage systems, passive sampling devices, SPMD, POCIS, DGT, seawater quality control, microcontaminants.

RESUMEN

Control de calidad del agua de mar para los micro-contaminantes en cultivos de peces en jaulas flotantes. Aplicación de dispositivos de muestreo pasivo

Las restricciones que imponen los países desarrollados al uso de sustancias químicas en la acuicultura para asegurar la salubridad de sus productos son cada vez mayores. También es creciente la preocupación por el control de los aditivos, residuos químicos o los preparados farmacéuticos que pudieran encontrarse en las partes comestibles de las especies acuícolas, así como la acumulación de micro-contaminantes en las mismas. En este trabajo se presenta un estudio sobre el uso de los sistemas de muestreo pasivo para los programas de control ambiental de las piscifactorías de jaulas flotantes. Se valora su capacidad de detectar niveles traza, la tasa de muestreo y la cinética de acumulación de micro-contaminantes. Se han probado los POCIS (Polar Organic Chemical Integrative Samplers) para detectar productos farmacéuticos, pesticidas y residuos hormonales, los SPMD (Semi-Permeable Membrane Devices) para detectar contaminantes bioacumulables y las membranas DGT (Diffusive Gradients in Thin films) para metales.

Palabras clave: *Jaulas flotantes, sistemas de muestreo pasivo, SPMD, POCIS, DGT, calidad de agua de mar, micro-contaminantes.*

INTRODUCTION

Development of monitoring programmes for environmental quality control is still one of the main concerns in marine aquaculture. The presence of microcontaminants is a recurring issue, and Directive 2000/60/EC is the framework under which pollutants considered as a priority must be controlled in any aquatic scenario (EC, 1998). However, chemotherapeutants, feed additives, or chemicals associated with structural materials are listed as compounds used in Mediterranean marine aquaculture (GESAMP, 1997; UNEP, 2004). The continued use of such chemicals in aquaculture could entail potential risks. The heavy use of antibiotics in seafood production is of recurring concern, since there is evidence that this may lead to the development of bacterial resistance in humans (FDA, 2003; ASM, 2000). Other compounds, such hormones or chemicals which mimic their action mechanisms, may change the reproduction functions of aquatic organisms. This is the case of surfactants, which are ingredients used in cleaning products (EDMAR, 2002). Chemicals whose use is not authorised by EU legislation are currently being used in some countries—such as malachite green, which reportedly has potential carcinogenicity and genotoxicity (EC, 1990; EFSA, 2005; Culp and Beland, 1996), but is still used for such varied purposes as fabric dye, to prevent fungal growth on fish eggs, and to treat parasitic infections in adult fish (EELA, 2004; Sanz, 2005). This concern regarding the use of chemicals is mainly related to long-term effects (antibiotic resistance, reproduction functions, or genotoxicity). Moreover, while some of these chemicals may be persistent and bioaccumulable in the trophic chain, others (e.g., antibiotics, herbicides, or some pesticides), although they are degradable in the environment, may be considered as persistent due to their continual use and consequent exposition of aquatic organisms. This awareness of the impact of such chemicals has led to the characterization and definition of environmental quality standards (EQS) for microcontaminants, highlighted in guidelines such as the Common Mediterranean Standards or Sustainability Standards (MAP, 2005).

Environmental monitoring programmes for microcontaminants are necessary to provide solid information which describes the main problems of chemical contamination for fish farm cage systems. Traditional water sampling methods (e.g., punctual or composite samples) is inappropriate because it requires large volumes of water to detect trace levels of chemicals, and cannot offer a complete assessment of contamination. Passive sampling devices are the integrative sampler, which provides time-weighted average concentrations of chemicals over deployment periods ranging from weeks to months. The two configurations of Polar Organic Chemical Integrative Samplers (POCIS), for generic and pharmaceutical chemicals, contain sorbent materials designed to maximise the types of polar chemicals sampled. Semi-Permeable Membrane Devices (SPMD) sample chemicals from the aqueous phase, mimicking the bioconcentration of organic contaminants in the fatty tissues of organisms. Diffusive Gradients in Thin films (DGT) integrate the available metal concentration during their deployment over several days.

POCIS, SPMD and DGT have been field-tested in several areas, such as in effluent wastewaters (Petty *et al.*, 2004; Buzier, Tusseau-Vuillemin and Mouchel, 2005; Stuer-Lauridsen and Kjølholt, 2000), rivers and lakes (Gimpel *et al.*, 2003; Sabaliunas *et al.*, 2003; Balmer *et al.*, 2004), or estuarine systems (Shaw and Müller, 2005). Potential target analytes to be sampled by those devices, such as pharmaceuticals and personal care products (PPCPs), pesticides, or anabolic steroids in water matrices (Álvarez *et al.*, 2005; Daughton and Ternes, 1999; Jones-Lepp *et al.*, 2001; Vermeirssen *et al.*, 2005), have been also tested. However, the use of these passive sampling devices for monitoring programmes in fish farm cage systems remains nonexistent or limited.

The present paper evaluates the effectiveness of passive sampling devices as tools in environmental monitoring programmes for fish farm cage systems. Capability to detect trace levels of microcontaminants, sampling rates and accumulation kinetic is assessed. Chemicals selected for this study include compounds which are used in aquaculture activities, as well as others from con-

tamination sources such as chemotherapeutants, pesticides, biocides, hormones, and metals.

MATERIALS AND METHODS

Standards, reagents and analytical systems

The following types of chemicals were selected to be tested by passive sampling devices. Biocides: Irgarol 1051 (2-methylthio-4-*tert*butylamino-6-cyclopropylamino-s-triazine) and TCMTB (2 thiocyanomethyl-*thio*-benthiazole). Hormones: estrone and 17α-ethinylestradiol. Pesticides: carbaryl terbutryn and dichlorvos. Fungicides: malachite green. Herbicides-algaecides: deltamethrin, permethrin, cypermethrin, simazine and atrazine. All the compounds were purchased from Sigma-Aldrich (Saint Quentin, Fallaviers, France) except Irgarol acquired from Dr Ehrenstorfer (Ausburg, Germany), and TCMTB, from Chemservice (Westchester, USA). All standards were of analytical grade (>90 %). $Cu(NO_3)_2.6H_2O$ was purchased from Riedel-Haen, Germany (purity >99 %). For Gas Chromatography-Mass Spectrometry (GC-MS) analysis, stock standard solutions of single compounds (100 mg/l) were prepared in methanol. A mixture stock solution at 10 mg/l was also prepared in methanol and stored at –20 ºC.

Residue analysis-grade n-hexane (95 %) and ethyl acetate (99.8 %) were supplied by Panreac (Barcelona, Spain), acetonitrile and methanol from Merck (Darmstadt, Germany).

Extractions of sampling devices membranes were performed using a Dionex ASE 200 Accelerated Solvent Extraction (Dionex, Idstein, Germany). Hydromatrix (pelletised diatomaceous earth) used for the pressurised solid-liquid extractions was purchased from Varian (Harbor City, CA, USA). For the clean-up step, minicolumns were packed with Florisil (MEGA BE-FL, 2 g, 12 ml, from Varian, Middelburg, Netherlands), and aminopropyl (Bondesil-NH_2, particle size: 40 μm, from Varian) as sorbent material.

Analysis of organic compounds was performed using the GC-MS system, and analysis of metals was carried out by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) HP 4500 Series. Data acquisition and instrumental control was performed by Chem-Station Software (Agilent Technologies, USA).

GC-MS analyses were run on a HP 6890 Series Gas Chromatograph (Hewlett-Packard, Palo Alto, CA, USA) interfaced to a HP 5973 Mass-Selective Detector. Data acquisition, processing and instrumental control were performed by Chem-Station software (Hewlett-Packard, USA). Analytes were separated in a Varian FactorFour capillary column VF-5ms (5 % diphenyl/95 % dimethylsiloxane), 30 m × 0.25 mm i.d., 0.25 μm film thickness. A split/splitless injector was used in pulse splitless mode. An empty liner was filled with glass wool (Agilent Technologies, USA) and placed at the end of the liner. The injector operating conditions were as follows: injection volume 10 μl; injector temperature 250 ºC; initial pulse pressure 30 psi (1.5 min). Helium carrier gas flow was maintained at 1 ml/min. The oven temperature programme was 4.0 min at 105 ºC, 17 ºC/min at 180 ºC, and 8 ºC/min at 290 ºC (5 min). Transfer line temperature was set at 270 ºC. Typical MS operating conditions were optimised by the auto-tuning software. Electron impact (EI) mass spectra were obtained at 70 eV electron energy and monitored from m/z 50 to 550. The ion source and quadrupole analyser temperatures were fixed at 230 ºC and 150 ºC, respectively.

An ICP-MS was used for the multi-element determination of trace heavy metals (Cu, Cd, Pb, Zn, Cr, Ni, As). Operating conditions were for plasma: incident power 1.3 kw, coolant gas flow rate Ar 15.0 l min^{-1}, auxiliary gas flow rate Ar 1.0 l min^{-1}, carrier gas flow rate Ar 1.0 l min^{-1}, sampling depth 5.5 mm from load coil. Nebuliser sample uptake rate: 0.1 ml min^{-1}.

Passive sampling devices and treatment of samples

Polar Organic Chemical Integrative Samplers (POCIS), Semi-Permeable Membrane Devices (SPMD) and Diffusive Gradients in Thin films (DGT) were tested for their application in environmental monitoring programmes involving fish farm cage systems.

POCIS devices were purchased from ExposMeter AB (Tavelsjö, Sweden), and consist of a sequestration medium enclosed within hydrophilic microporous polyethersulfone membranes for integrative sampling of polar organic chemicals. Figure 1 shows a scheme of POCIS design. A detailed description of this sampling technology has been published previously (Álvarez *et al.*, 2004; Website a). Two configurations of POCIS were used in this study: the generic configuration contains a mixture of three sorbent materials to sample most pesticides, natural and synthetic hormones, many wastewater-related chemicals, and other water-soluble organic chemicals; the pharmaceutical configuration contains a single sorbent material designed for sampling most pharmaceutical groups.

SPMD devices were supplied by ExposMeter AB, and consist of thin layflat semipermeable polyethylene tubing (2.54 cm × 91.4 cm) which contain 1.0 ml of triolein. The preparation and composition of SPMD devices has been described in detail elsewhere (Petty *et al.*, 2000; Website b). Potential target analytes sampled by SPMDs include hydrophobic and bioaccumulable organic chemicals.

DGT membranes purchased from ExposMeter AB use a layer of Chelex resin impregnated in a hydrogel designed to accumulate metals. The resin layer is overlaid with a diffusive layer to reach the resin layer. Figure 1 also shows an example of DGT design. The preparation and composition have been previously described (Denney, Sherwood and Leyden, 1999; Website c).

A general procedure was developed for the extraction of microcontaminants from membranes of POCIS and SPMD sampling devices using a Dionex ASE 200. For POCIS devices, 11 ml stainless-steel extraction cells were used, and for SPMD, 22 ml cells. For an effective extraction step, membranes and Hydromatrix were placed inside the cells, and a cellulose filter was placed in the upper part of the cells.

For the extractions of polar organic chemicals sampled by POCIS devices, a pressurised solid-liquid extraction procedure was carried out. For pharmaceutical POCIS, three cycles of extraction with a mixture of acetonitrile and methanol (50:50) were programmed, using the following conditions: oven temperature, 40 ºC; extraction pressure, 1 000 psi; static time, 5 min; and flush volume, 60 %. For generic POCIS, three cycle of extraction with solvents, acetonitrile and methanol (50:50) were also carried out under the following conditions: oven temperature, 100 ºC; extraction pressure, 1 500 psi; static time, 5 min; and flush volume, 60 %.

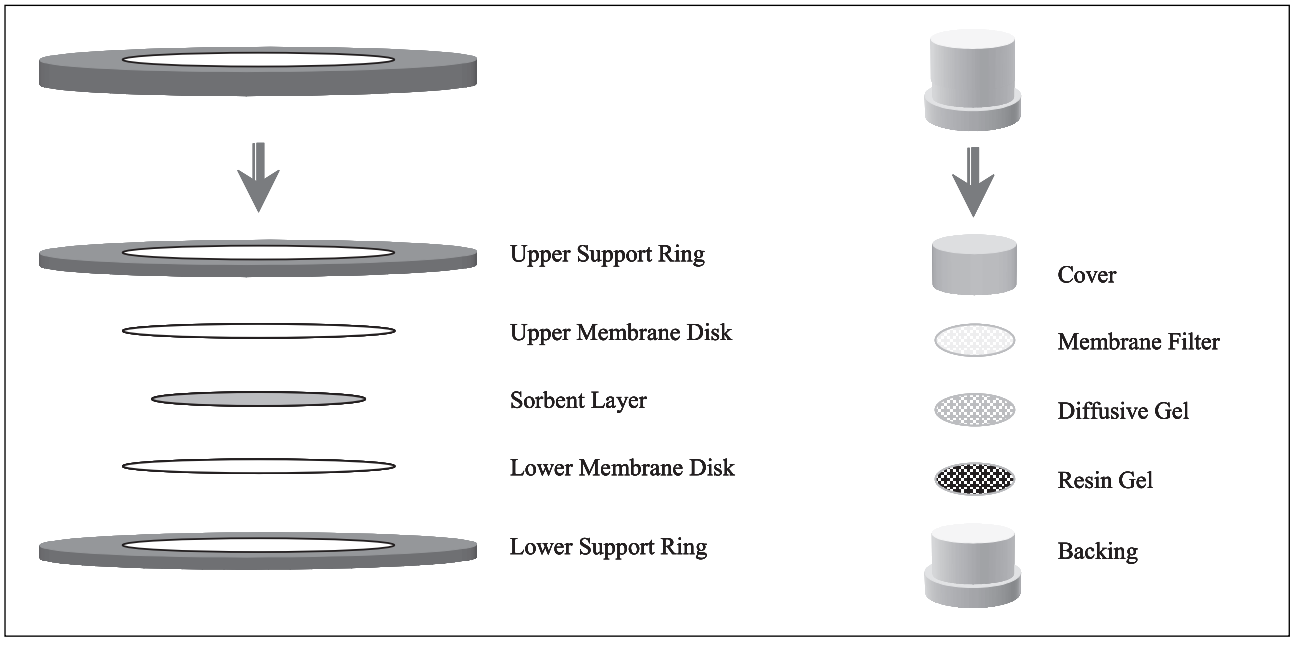

Figure 1. Scheme of POCIS and DGT design

Extraction of nonpolar organic chemicals from SPMD devices was performed with three cycles of pressurised solid-liquid extraction processes using n-hexane as solvent, and under the following conditions: oven temperature, 50 ºC; extraction pressure, 1 000 psi; static time, 5 min; and flush volume 60 %.

The extracts were collected in pre-cleaned 30 ml glass vials and carefully concentrated by evaporation of solvent with gentle nitrogen stream to a final volume of 2 ml. A clean-up step was then applied. For that, extracts were transferred to a glass mortar containing 2 g of aminopropyl. The homogeneous mixture was introduced into a minicolumn that was packed with 2 g of florisil. Then, the analytes were eluted from the SPE cartridge with 10 ml of organic solvent (n-hexane for SPMD and acetonitrile for POCIS). Finally, the eluates were dried with nitrogen and reconstituted in 200 µl of ethyl acetate, except for those from the SPMD, which were dried to 1 ml. Thus, the pre-concentration factor of extracts from POCIS and SPMD devices was 70 and 25, respectively. Before injection by GC-MS system, the extracts were filtered through a 0.45 µm PTFE filter (Millipore, USA).

For DGT extraction, the cover device was carefully opened, and the resin layer was retrieved and placed inside a clean centrifuge tube of 15 ml. Then, the resin was immersed in 1 ml of 1 M HNO_3 solution for 24 hours. Before analysis by ICP-MS, a dilution of sample was performed adding 9 ml of deionised water.

Validation studies

To evaluate the use of passive sampling devices as effective tools in environmental monitoring programmes for fish farm cage systems, their capability to detect trace levels of micro-contaminants, sampling rates and accumulation kinetic was studied.

The capability to detect trace concentration levels was evaluated by determining the method detection limits (MDL) obtained from instrumental limits of detection (LOD) and the pre-concentration factor of sampling extract, as well as the accumulation of chemicals achieved by passive sampling devices. LOD were determined from the injection of spiked seawater extract (n = 6 replicates) and calculated using a signal-to-noise ratio of 3. The pre-concentration factor of sampling extracts from POCIS and SPMD devices was 70 and 25, respectively. To determine the accumulation of chemicals in passive sampling devices, sampling rates were calculated.

The sampling rate (Rs) measures the volume of water which is cleaned of target analytes per time unit (Álvarez *et al.*, 2000). In other words, this parameter makes it possible to determine the concentration in natural water from the concentration detected in the membrane (SPMD and POCIS) and was calculated according to the following equation:

$$R_S = \frac{M}{C \times t}$$

where M is the mass of analyte accumulated by the membrane, C is the mean concentration in the water during the measurement, and t is the sampling period.

For determining sampling rates of target analytes, an experiment was designed in the laboratory. The passive sampling devices were placed in single glass containers with a volume (20 l) of seawater spiked with the target chemicals. For POCIS and SPMD devices, seawater was spiked with the target organic chemicals at a concentration of 170 ng/l. The experiment was carried out under constant turbulence, a temperature of 18 ºC, and during exposition periods for the samplers of 18 and 24 days. From the concentration detected in POCIS devices, the accumulation kinetic for target organic analytes was evaluated.

In the case of DGT devices, a constant concentration gradient in the diffusive layer is produced, and is the basis for measuring metal concentrations in solutions quantitatively without any need for separate calibration. A similar experiment for determining sampling rates in POCIS and SPMD was performed to determine the pre-concentration factor of Cu element in DGT. To do this, seawater was spiked with $Cu(NO_3)_2.6H_2O$ at 20 ng/l under similar conditions, with constant turbulence and a temperature of 18 ºC. The following equation was applied to calculate the concentration of metal in the solution (C) from the

measured mass of metal accumulated in the resin for a determined deployment time:

$$C = \frac{M \times \Delta g}{D \times t \times A}$$

where M is the measured mass of metal accumulated in the resin gel, Δg is the thickness of the diffusive gel (0.8 mm) plus the thickness of the filter membrane (0.13 mm), D is the diffusion coefficient of each metal in the gel, t is deployment time, and A is the exposure area (A = 3.14 cm^2).

RESULTS

Capability to detect trace concentration levels of chemicals in seawater

Sensitivity to detect trace concentration levels of organic chemicals in seawater was evaluated by determining the method detection limits (MDL) of the target chemicals. To do this, instrumental limits of detection (ILOD) and the pre-concentration factor of sampling extracts, as well as accumulation of chemicals achieved by passive sampling devices, was determined. ILOD were determined from the injection of spiked seawater extract with the target analytes. Figure 2 shows a GC chromatogram corresponding to a spiked seawater extract with target microcontaminants at 50 µg/l. The GC-MS system was operated in EI mode to obtain enhanced selectivity and sensitivity. Analysis was performed using selected ion monitoring (SIM) mode, where ions are monitored to identify the analytes of interest in samples. Three ions were used to identify the target analytes, and among these, the most abundant ion in the mass spectrum was selected for quantitative purposes. The selection of identification ions was based on high relative abundance and high value m/z of fragment ions from the mass spectrum. Criteria to identify target analytes were the presence of three identification ions, relative abundance of identification ions (within 20 % relative standard variation, RSD), and retention time. Table I

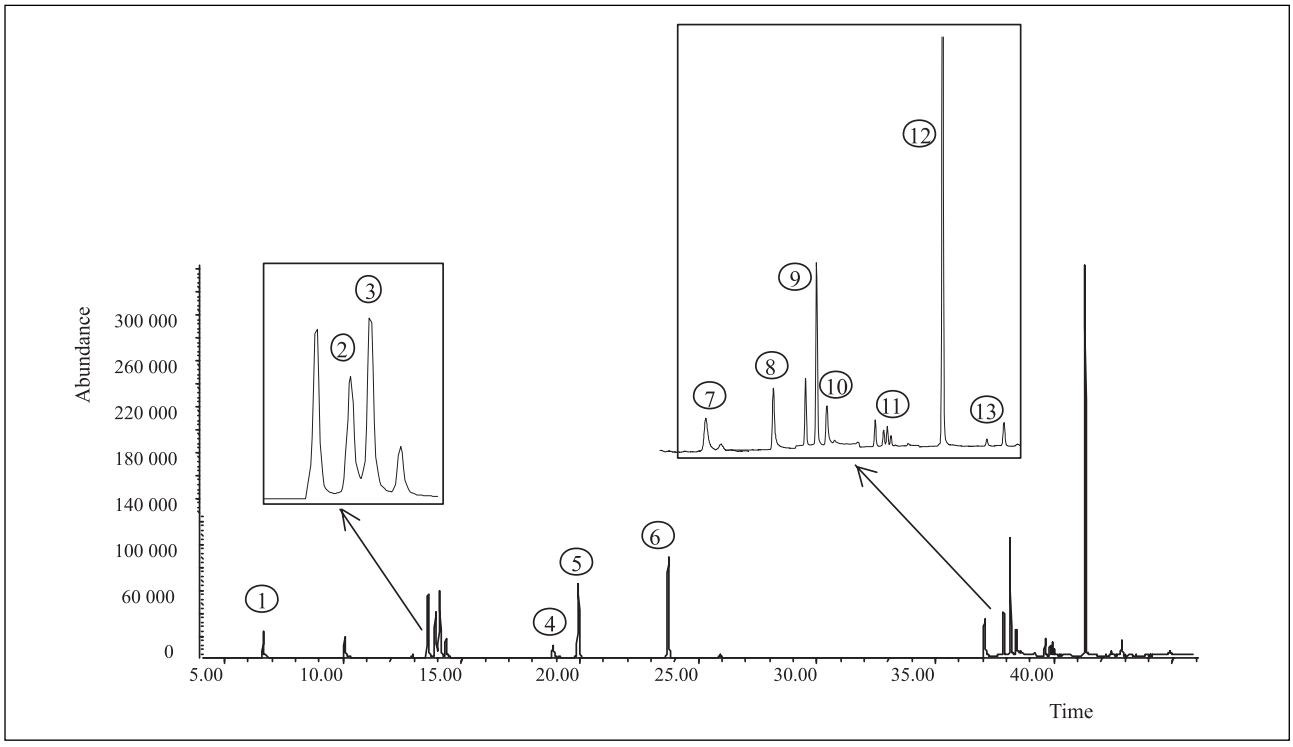

Figure 2. GC-MS chromatogram of spiked seawater extract with target microcontaminants at a concentration of 50 µg/l: (1) dichlorvos, (2) simazine, (3) atrazine, (4) carbaryl, (5) terbutryn, (6) irgarol, (7) TCMTB, (8) estrone, (9) permethryn, (10) 17α-ethinylestradiol, (11) cypermethrin, (12) malachite green, (13) deltamethrin

shows the identification and quantification ions used in the analysis of target analytes. The ILOD achieved were in µg/l for the selected compounds (0.9-38.7 µg/l). However, due to the high dilution factor in a marine environment, concentration of chemicals can be in low ng/l, and instrumental sensitivity to detect trace levels is not sufficient. The pre-concentration factor of sampling extracts obtained from the extraction step of membranes to the sample preparation for analysis by GC-MS was 70 for POCIS and 25 for SPMD.

The accumulation of chemicals in passive sampling devices was derived from the experiments for determining sampling rates. From the experiment performed under controlled conditions, the concentration of selected chemicals detected in the membrane was calculated according to the formula described in section 2.2. Table I summarises the MDL obtained using POCIS and SPMD for the target analytes. With those sampling devices, concentration levels of low ng/l could be detected in a marine environment. In particular, in the generic mode of POCIS, chemicals are detected from 0.2 to 43 ng/l; in the pharmaceutical POCIS, 0.1-38 ng/l; and for SPMD, from 0.4 to 89 ng/l. Thus, in general the sensitivity achieved by applying passive sampling devices could be suitable to detect trace levels (low ng/l) in a marine environment. On the other hand, similar selectivity and sensitivity were observed for most chemicals selected to be studied by the two POCIS configurations. Even though the POCIS pharmaceutical configuration is designed for those compounds, other chemicals, such as pesticides or biocides, can be sampled with this device. However, because this configuration is designed for most pharmaceuticals, compounds with a wide polarity could be also sampled.

The sensitivity to detect trace levels of inorganic compounds in seawater was also evaluated, determining the MDL. The ILOD for the selected heavy metals was in µg/l (0.1-0.3) and therefore, given that the environmental concentration in a marine environment is even lower, preconcentration of the sample is a necessary step. Under the conditions used in the experiment for determining accumulation of Cu in DGT, the pre-concentration achieved was 56. Thus, sensitivity is enhanced, and the MDL of Cu element is in ng/l (18 ng/l).

Sampling rate and accumulation of chemicals

For determining the accumulation of chemicals in passive sampling devices, sampling rates were calculated for the selected chemicals. Environmental factors, such as flow/turbulence regimes or temperature, determine the sam-

Table I. Sensitivity: instrumental and methods limit of detection (ILOD, MLD) for microcontaminants. Identification and quantitation ions in GC-MS analysis. (*): quantitation ions (m/z) are underlined

Organic compounds	t_R	Identification/ quantitation ions* (m/z)	ILOD GC-MS (µg/l)	Passive sampling devices					
				MDL POCIS Generic (µg/l)	MDL POCIS Pharmac (µg/l)	MDL SPMD (µg/l)	Elements	ILOD ICP-MS (µg/l)	MDL DGT (µg/l)
Dichlorvos	6.6	<u>109</u>, 145, 185	6.6	0.006	0.009	0.077	Cr	0.3	0.053
Carbaryl	12.9	115, <u>144</u>, 145	3.2	0.003	0.004	0.036	Mn	0.1	0.018
Simazine	14.1	186, <u>201</u>, 203	3.5	0.012	0.011	0.031	Co	0.1	0.018
Atrazine	18.8	<u>200</u>, 202, 215	2.3	0.007	0.007	0.024	Ni	0.1	0.018
Terbutryn	19.9	185, <u>226</u>, 241	1.5	0.005	0.005	0.016	Cu	0.1	0.018
Irgarol	23.7	182, 238, <u>253</u>	4.8	0.013	0.011	0.043	Zn	0.1	0.018
TCMTB	25.9	166, <u>180</u>, 238	7.7	0.012	0.006	0.031	As	0.1	0.018
Estrone	37.3	185, 213, <u>270</u>	3.8	0.004	0.004	0.013	Cd	0.1	0.018
Permethrin	38.1	163, 165, <u>183</u>	13.4	0.015	0.012	0.034	Pb	0.2	0.036
17α-Ethinylestradiol	38.7	213, 228, <u>296</u>	30	0.043	0.038	0.086			
Cypermethrin	40.2	<u>163</u>, 165, 181	42	0.035	0.032	0.089			
Malachite green	41.5	165, 253, <u>330</u>	0.9	0.0002	0.0001	0.0004			
Deltamethrin	43.1	181, 209, <u>253</u>	38.7	0.010	0.010	0.019			

pling rates of chemicals, and theoretical models can describe the sampler performance. With the experiment described above performed at constant turbulence and a temperature of 18 °C, an estimation of sampling rates was obtained for these conditions. The temperature selected was 18 °C in order to approximate environmental conditions in seawater during the spring-summer period. Other environmental factors, such as biofouling, could also reduce the accumulation of chemicals in the membranes; however, those devices are resistant to fouling for a determined exposition period, and may also be cleaned of sediments and particulate matter.

Rates of chemical uptake for polar compounds are generally controlled by diffusion across an aqueous boundary layer at the membrane surface in POCIS. In the case of SPMD, dissolved and readily bioavailable organic contaminants diffuse through the membrane and are concentrated over time. In this device, the sequestration media consist of neutral lipid triolein where contaminant residues are concentrated in SPMD simulating the bioconcentration of organic contaminants in fatty tissues.

Sampling rates of target chemicals were determined at two period of exposition, 18 and 24 days (table II). Under experimental conditions, similar behaviour for the target chemicals which were sampled using the generic and pharmaceutical POCIS was observed for both exposition periods. Between the POCIS configuration devices, the only noticeable difference was observed in the sampling of TCMTB, where the sampling rate was smaller using the POCIS generic configuration than the pharmaceutical one. The same sort of pattern was also observed in SPMD sampling rates for 18 and 24 days. However, considering SPMD and POCIS, in general, sampling rates for polar compounds were higher using SPMD than using POCIS, and similar for apolar compounds.

Accumulation of chemicals by passive samplers typically follows first-order kinetics, where analyte uptake is linear. This initial phase is characterised as an integrative phase which is followed by curvilinear and equilibrium partitioning phases. Therefore, these devices provide an estimate of the time-weighted average (TWA) concentration of contaminants during a specified exposure period. Figure 3 shows the accumulation of chemicals achieved in POCIS membrane at 18 and 24 days of exposition. Under these conditions, the accumulation profile was different for different chemicals. For example, regarding compounds such as simazine or Irgarol, accumulation is still in the initial phase and sampling period could be extended in the time. On the other hand, for compounds such as deltamethrin, dichlorvos or carbaryl, accumulation at 18 and 24 days is quite similar, and is probably the curvilinear phase, indicating that an optimal period of sampling could be achieved.

Table II. Sampling rates for target organic compounds in POCIS and SPMD devices at two periodd of exposition (18 and 24 days)

Organic compounds	18 days			24 days		
	POCIS Generic	POCIS Pharmaceuticals	SPMD	POCIS Generic	POCIS Pharmaceuticals	SPMD
Dichlorvos	0.015	0.021	0.086	0.013	0.021	0.098
Carbaryl	0.016	0.019	0.098	0.014	0.019	0.095
Simazine	0.049	0.042	0.089	0.049	0.045	0.074
Atrazine	0.042	0.043	0.084	0.042	0.042	0.084
Terbutryn	0.049	0.047	0.095	0.045	0.043	0.090
Irgarol	0.033	0.042	0.087	0.041	0.032	0.073
TCMTB	0.016	0.005	0.035	0.023	0.011	0.033
Estrone	0.012	0.013	0.029	0.016	0.015	0.028
Permethryn	0.015	0.011	0.026	0.017	0.013	0.021
17α-Ethinylestradiol	0.026	0.023	0.029	0.021	0.018	0.024
Cypermethrin	0.009	0.006	0.017	0.012	0.011	0.017
Malachite green	0.002	0.003	0.004	0.003	0.002	0.004
Deltamethrin	0.005	0.004	0.005	0.004	0.003	0.004

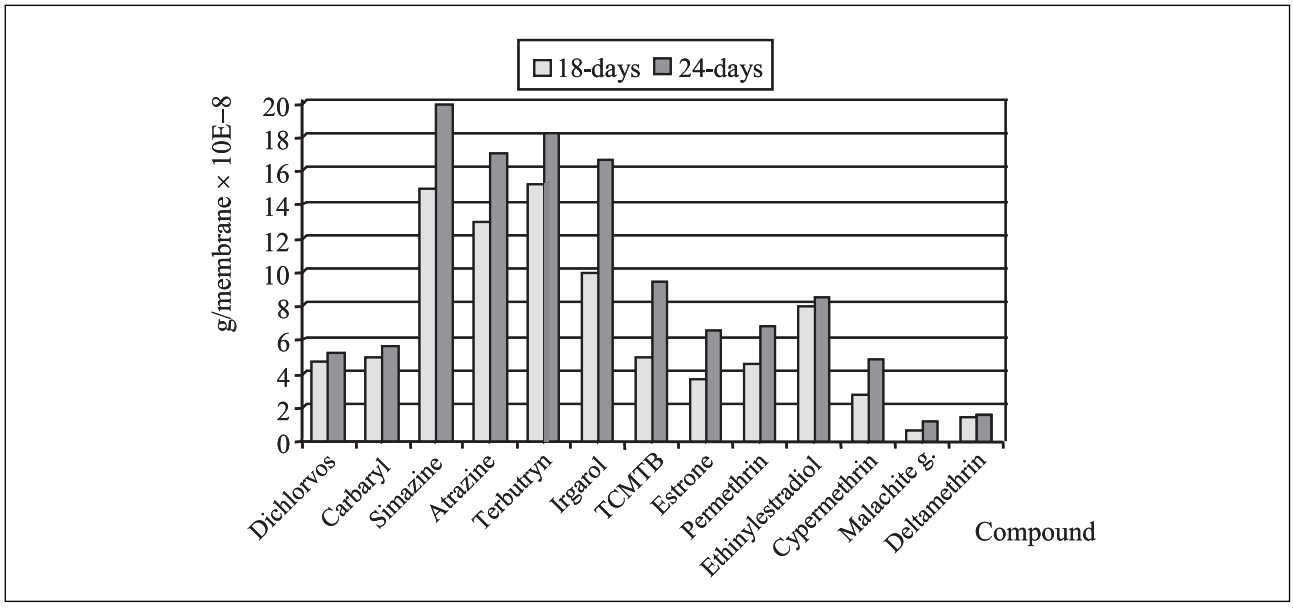

Figure 3. Accumulation of microcontaminants in POCIS at two periods of exposition (18 and 24 days)

CONCLUSIONS

The passive sampling devices tested in the present study –POCIS, SPMD, and DGT– are all suitable for detecting trace concentration levels of microcontaminants in a marine environment. Accumulation behaviour of target chemicals, such as pesticides and biocides, is similar in both POCIS configurations, under experimental conditions. Optimal sampling period was achieved at 18 or 24 days for most target compounds. These preliminary results are part of a larger research study which is being developed for designing optimal microcontaminant parameters and sampling frequencies to be used in environmental monitoring programmes for fish farm cage systems.

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