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Comparing the Passive and Active Sampling Devices with Biomonitoring of Pollutants in Langstone and Portsmouth Harbour, UK

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Abstract: Two types of integrative sampling approaches (passive samplers and biomonitors) were tested for their sampling characteristics of selected pollutants. Chemical analysis by gas chromatography with mass spectrometry (GC/MSD) were used to determine the amounts of eight compounds (diuron, γ -HCH, atrazine, irgarol, phenanthrene, dieldrin and two congeners of polychlorinated biphenyls; PCB 52 and PCB 153) in two passive sampling devices (Chemcatcher and Ecoscope) and marine mussels (*Mytilus edulis*), both had been deployed in Langstone and Portsmouth Harbour, UK. Diuron, irgarol, atrazine and phenanthrene were determined in spot samples of the two deployment sites (Haslar marina and Port Solent) during field trial. All the compounds except the dieldrin have been detected by Chemcatcher passive samples and mussels. Ecoscope passive samples had the ability to detect diuron and irgarol with lower concentration (1.5 and 22.4 ng L⁻¹, respectively) than detected by Chemcatcher passive samples (1500 and 125 ng device⁻¹) in port Solent after 14 days of the deployment. The study proved that Chemcatcher passive samples and biomonitoring organisms may provide complementary information since, the former samples only the free fraction and the latter both the free and particulate-bound fractions of pollutants in aquatic environments. The Chemcatcher samples has been proved that it can overcome some of the deficiencies of existing devices such as Ecoscope passive samples and to cover a wide range of polarities. It proved also to be the preferred method for assessing the presence of these compounds since, employing mussels had several disadvantages both in sampling efficiency and sample analysis.

Key words: Chemcatcher and Ecoscope passive samplers, biomonitor, *Mytilus edulis*, polychlorinated biphenyls, pesticides, water, pollution

INTRODUCTION

The Chemcatcher passive sampling device was developed by Portsmouth University in the frame of an EU project (Standardized Aquatic Monitoring of Priority Pollutants by Passive Sampling, STAMPS). It consists of the basic configuration of aquatic passive samplers being formed by a receiving phase with high affinity for organic chemicals which is separated from the environment by a diffusion limiting membrane. In this case, both the receiving phase and the diffusion membrane are 47 mm diameter disks, loaded on a rigid

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polytetrafluoroethylene (PTFE) body. It was designed in order to enable its application to several classes of target analytes by simply varying the receiving phase and the membrane in accordance with the compounds affinities. A complete description of the device can be looked up in Kingston *et al.* (2000), Vrana *et al.* (2006) or Greenwood *et al.* (2007). These researchers developed the system and calibrated its use for the detection of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), organochlorine pesticides and triazines.

Passive sampler could provide the solution to problems associated with costly and time consuming sampling programmes and biomonitoring. Mussels (*Mytilus edulis*) and Chemcatcher passive sampler were simultaneously analyzed for sequestered pesticides and polychlorinated biphenyls (PCBs) by gas chromatography with mass spectrometry (GC/MSD) in the laboratory trail (El-Shenawy *et al.*, 2009). The Chemcatcher passive sampler based on a solid phase extraction disc with two types of diffusion-limiting membranes (polyethelene and polysulphone), were also compared. Diuron, atrazine, irgarol and lindane were accumulated in the polysulphone passive sampler in greater concentration than in the mussels or in the other passive samplers with polyethelene limiting-membrane. Mussels can accumulate in their tissue high concentration of non polar compounds such as PCB 52, dieldrin and PCB 153, more than the passive sampler with polysulphone membrane. The Chemcatcher passive sampler with polyethelene limiting membrane has high affinity for phenanthrene, dieldrin, PCB 153 and PCB 52, so it acts as a sampler for non-polar compounds (El-Shenawy *et al.*, 2009). The design and field performance of a wide range of passive samplers suitable for monitoring organic pollutants have recently been reviewed (Namiesnik *et al.*, 2005; Stuer-Lauridsen, 2005; Vrana *et al.*, 2005a). Chemcatcher has been tested in the laboratory for measurement of Time Weighted Average (TWA) concentrations of pollutants in aquatic environments (Kingston *et al.*, 2000; Vrana *et al.*, 2005b; El-Shenawy *et al.*, 2009; Greenwood *et al.*, 2009) and its bioaccumulation could provide robust and reliable information at relatively low cost compared to biomonitoring data. The sampler is based on the diffusion of target compounds through a membrane and the subsequent accumulation of these pollutants in a sorbent-receiving phase. Accumulation rates and selectivity are regulated by the choice of both the membrane and a receiving phase material (Vrana *et al.*, 2007). One of the prototypes was designed for the sampling of non-polar organic compounds with log octanol/water partition coefficient ($\log K_{ow}$) values greater than three (Kingston *et al.*, 2000; El-Shenawy *et al.*, 2009). This system used a 47 mm C18 Empore disk as the receiving phase and a low density polyethylene (LDPE) membrane. The C18 Empore disk has a high affinity and capacity for the sampled pollutants.

In this study, we compared the efficacy of marine mussel as a biomonitor and two passive sampling devices (Chemcatcher and Ecoscope commercial device) during deployment for measurement of time-averaged concentration of organic pollutants in aquatic environment using sites in Langstone and Portsmouth Harbour to evaluate the performance of the Chemcatcher sampler. These sites were expected to contain biocides used in anti-fouling treatments, though at levels which fluctuated depending on the state of the tide. All three sites might be expected to contain low levels of industrial micropollutants and stable pesticides such as the cyclodienes and atrazine. An empirical relationship that enables the calculation of *in situ* sampling rates of non-polar chemicals using Performance Reference Compounds (PRCs) was derived. Its application was demonstrated in a field study in which sampler data were compared with spot samples of water, collected regularly during the sampler deployment.

MATERIALS AND METHODS

Materials and Chemicals

C₁₈ Empore disks (47 mm diameter) were purchased from Varian Inc., Walton-on-Thames, UK. Low density polyethylene (LDPE) membrane material (40 mm thickness) was obtained from Fisher Scientific, Loughborough, UK. Soxhlet apparatus which are quickfit glassware with cellulose thimbles (Whatman Ltd, England), were used in extraction of pollutants from mussels. The solvents (HPLC grade quality or equivalent), acetone, ethyl acetate, methanol, hexane, octanol, nonane, 2, 2, 4-trimethyl pentane and water were obtained from Fisher Scientific. Certified pure (purity>98% in all cases) reference standards of the test compounds, surrogates and internal standards were obtained from Qmx Laboratories, Saffron Walden, UK.

Field Deployment of Samples

In choosing the deployment sites two criteria were used. Firstly, the chosen site should provide both access for the regular spot sampling and a degree of security so that the sampler would not be disturbed. Secondly, the sites should be sufficiently contaminated with target pollutant to allow accurate quantization using the available equipment. Port Solent and Haslear marinas were used as deployment sites that were identified in the enclosed Portsmouth Harbour (Fig. 1A, B). Both marina sites are used mainly for the mooring of small ocean-going vessels. Although, both sites are essentially fed by the same water, i.e seawater from the Solent, the marina at Haslar is suited at the mouth of the Harbour and Port Solent marina is suited at the head of the harbour. The latter is more enclosed site than the former and it is anticipated that the difference in water exchange rates at the two sites would be reflected in different average contamination levels fluctuations around these means. A third reference site was chosen at the Portsmouth raft site in Langston Harbour, Portsmouth (Fig. 1C). The samplers and bags of mussels were attached to the paint-testing rafts in Langston channel. These floating structures harbour have been immersed at the site in one of the main channels for more than 30 years. At this site the minimum depth of water is 4 m and there is a tidal current throughout most of the tidal cycle. The rafts were 19 m long by 7 m wide, constructed of metal tanks with two main central basins into which the test panel frames are immersed. The caged animals and passive samplers were retrieved at the same time in all the sites. A suite of organic pollutants (dieldrin, gamma-hexachlorocyclohexane (γ -HCH), polychlorinated biphenyls (PCBs) congeners No. 52 and 153, diuron, irgarol, atrazine and phenanthrene were analyzed.

Initial screening of the marine sites confirmed the presence of two biocides used commonly in antifouling paint formulations; these were diuron and irgarol 1051. The majority of commercially available antifouling paints contain biocides to prevent the growth of algal and bacterial slimes on surfaces submerged in environmental water. The paint structure is such that biocides contained within the paint leach slowly from the paint surface and are released into the surrounding water. High levels of biocides present at the paint/water boundary produce a toxic layer at the surface which reduces the rate of attachment and growth of biofouling organisms. Antifouling paints are applied to the hulls of the yachts and dingys moored in the Solent and Portsmouth Harbour area.

Calibration Data

The calibration data were obtained in experiments designed to measure the uptake of target analytes and offloading of PRC at different combinations of temperature and

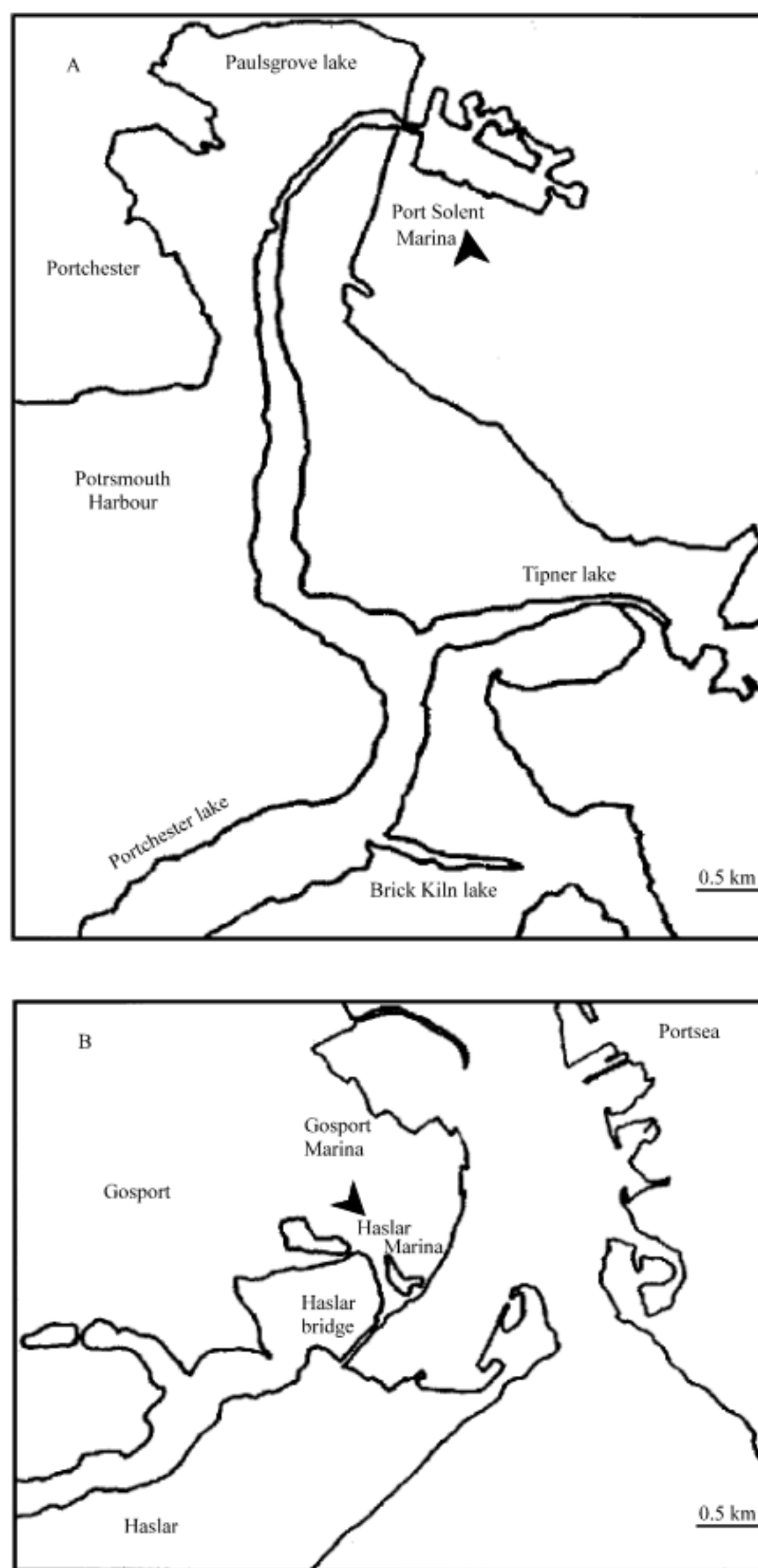


Fig. 1: Continued

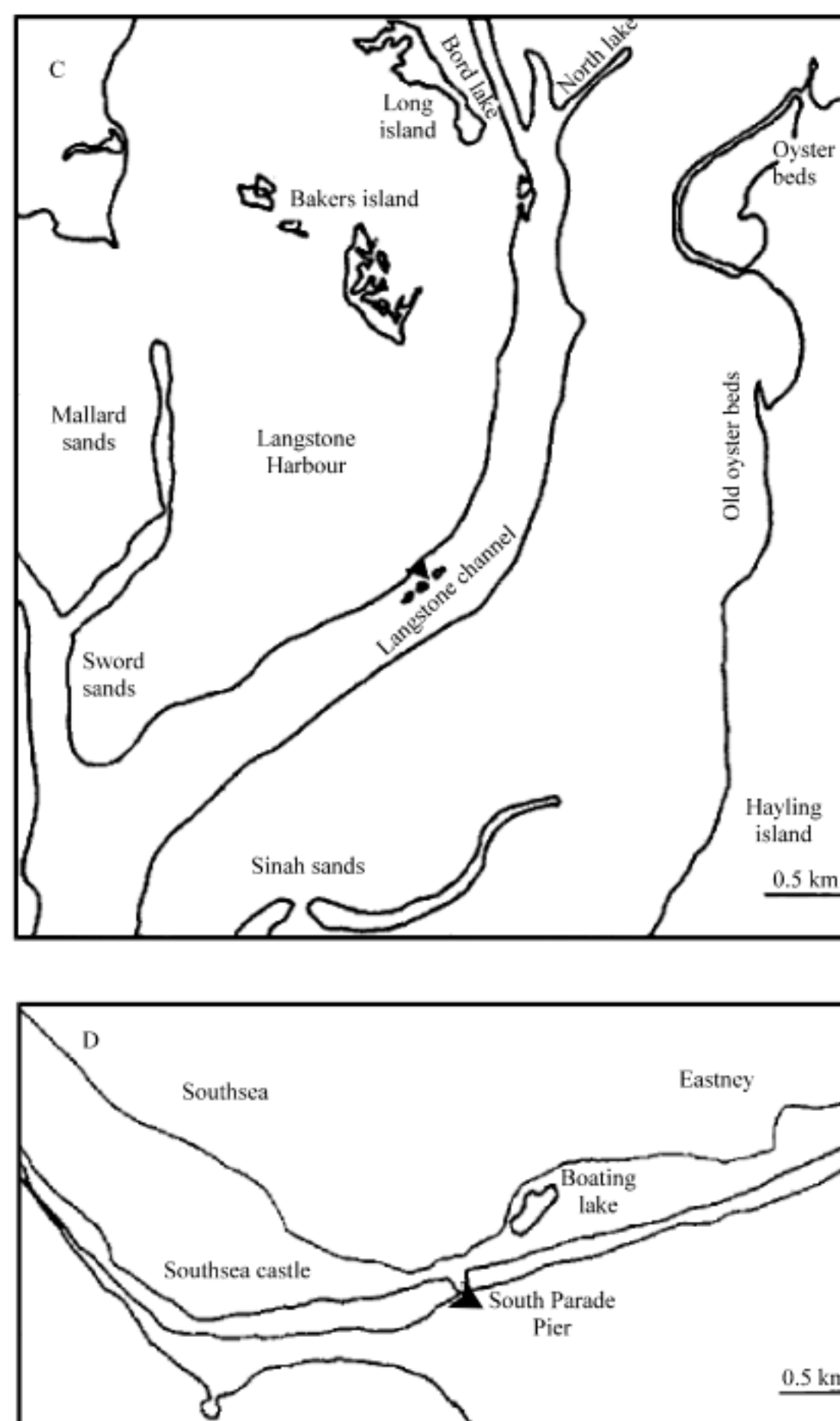


Fig. 1: Location of field trail in Portsmouth Harbour, UK (A) Port Solent Marina, (B) Haslear Marina, (C) location of reference site in Langston Harbour and (D) location of collection site (South Parade Pier on the shore of Southsea, Portsmouth) of marine mussel, *Mytilus edulis*

hydrodynamic conditions in a full factorial design. The calibration data were gathered in order to determine the sampling parameters for uptake of target analytes (sampling rate; RS) and for the offload of PRCs (overall exchange rate constants; k_e) and to observe how they are affected by environmental conditions. Briefly, in each experiment up to 14 passive samplers were exposed for up to 14 days in a constant concentration flow-through exposure system, under controlled conditions of temperature, water turbulence and analyte

concentration. Each factor (temperature, stirring speed) was tested at three levels, resulting in the total number of nine experiments. The experiments have been described in detail and the calibration data reported (Vrana *et al.*, 2006; El-Shenawy *et al.*, 2009).

Samples Preparation

Chemcatcher Passive Sampler

This passive sampling device consisted of a C₁₈ Empore disc as chromatographic receiving phase and a 0.2 µm pore size polysulphone (ps) or 10 A polyethylene (pe) pore diameter as diffusion-limiting membrane (El-Shenawy *et al.*, 2009). The C₁₈ Empore (47 mm inner diameter) discs (manufactured by 3 M) required conditioning prior to their use as receiving phase for the passive sampling system. The conditioning process consists of soaking the disks in HPLC grade methanol (10 mL) (Fischer Scientific) for 20 min in a glass beaker. During this time the disks take on a translucent appearance. The disks are transferred to a glass beaker containing ultrapure water to remove excess methanol. The disks are removed from the water and excess water was removed by dry tissue. The disks are now ready for deployment into the body of the passive sampling device. The methanol removes any contamination from the disk and solvates the sorbent phase increasing its ability to sequester organic analytes. For this reason it is important not to let the C₁₈ disks dry out at any stage between conditioning and deployment of the passive sampling device (Vrana *et al.*, 2006).

The main body of the sampler consists of three components all manufactured from polytetrafluoroethylene (PTFE) and a chromatographic receiving phase separated from the aquatic environment by a diffusion limiting membrane. The chromatographic phase followed by the diffusion limiting membrane is placed on the thin rigid supporting disc (50 mm diameter, 5 mm thickness) of PTFE. The diffusion limiting membrane is placed over the C₁₈ disc and any visible air bubbles are smoothed away from between the two membranes. On the opposite face the supporting disc has a machined round lug (10 mm long and 5 mm inner diameter) of PTFE with a small hole (3 mm inner diameter) drilled completely through so that the device can be suspended during field sampling either by wire or nylon cord. The loaded supporting disc (with chromatographic phase and diffusion limiting membrane) is carefully inserted by hand into the locating ring of the front segment of the PTFE body. Holding the supporting disc in the position the rear segment of the PTFE body is carefully screwed into the front segment of the body to form a watertight seal between the outer face of the diffusion limiting membrane and the front segment of the body (Vrana *et al.*, 2005b; El-Shenawy *et al.*, 2009).

The loaded passive samplers are stored submerged in ultrapure water and sealed in glass jars. The device is lowered into the water and any air trapped in the front face of the sampler body is removed by briefly inverting the assembly. The device is then allowed to hang freely in the water. The device naturally hangs with the exposed face of the diffusion limiting membrane pointing downward.

The samplers were prepared in the laboratory and taken in glass jars filled with ultrapure water to the deployment sites (Fig. 2A). Six samplers were deployed in close proximity at each of the chosen sites. The samplers were suspended in a vertical orientation at a depth of 10-20 cm using coloured nylon thread with the diffusion limiting membrane facing downwards to minimize the settlement of silt during the deployment period. Three replicate Chemcatcher samplers were deployed for 14 days from 23rd February to 5th March 1999. During the exposure, the water temperature at the sampling site varied from 6.5 to 8.0. After the required deployment period the device is taken from the sampling site and disassembled.

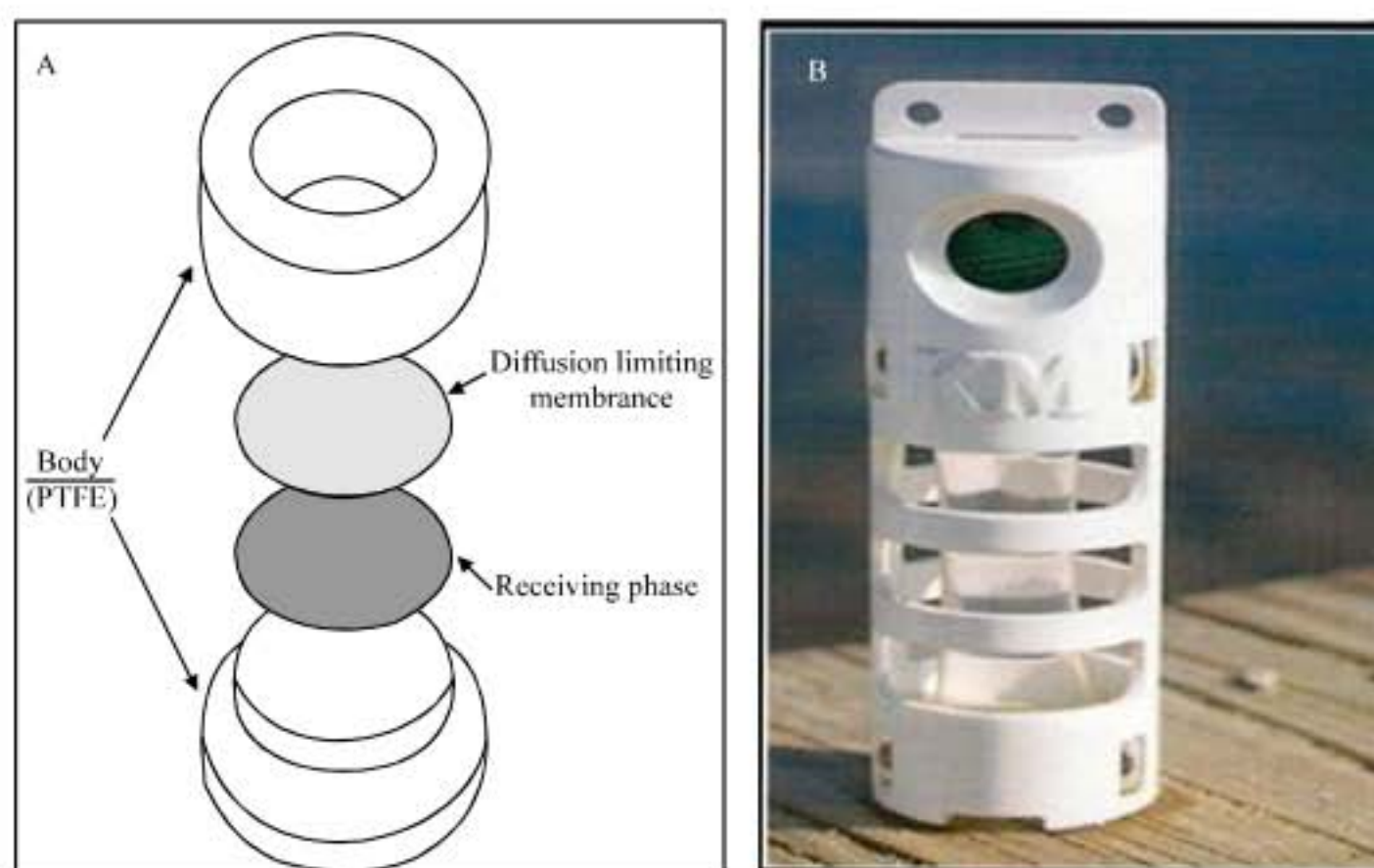


Fig. 2: (A) Chemcatcher general configuration and (B) the Ecoscope passive sampler (Km Lab, Sweden) used in field

Disassembly follows the reverse of that described above for assembly. The chromatographic receiving phase is removed using clean stainless steel forceps and is placed in a clean glass screw top vial fitted with a PTFE lined cap. The chromatographic phase is stored at -20°C until analysis. The diffusion limiting membrane is discarded. The PTFE body and supporting disc are washed with water and organic solvent prior to reuse.

The organic determinants (diuron, γ -HCH, atrazine, irgarol, phenanthrene, dieldrin, PCB 52 and PCB 153) were extracted from the C_{18} Empore disks by means of ultrasonicing for 5 min in 5 mL of HPLC grade acetone followed by 5 min in 10 mL of 50:50 (v/v) ethylacetate: 2, 2, 4-trimethylpentane. At the end of this time, the disk was removed and the two solvent extracts were combined and $100\ \mu\text{L}$ of the $1\ \text{ng}\ \mu\text{L}^{-1}$ solution of ^{10}D -phenanthrene added as an internal standard to correct for volumetric inaccuracies during sample preparation. The extract was concentrated to a volume of 1 mL under a stream of nitrogen and the extract was placed into 2 mL autosampler vials in preparation for determination with a 6890A series gas chromatography equipped with mass-selective detector 5973 (GC-MSD, Agilent Technologies, Bracknell, UK) (Vrana *et al.*, 2005b). The gas chromatographic (Hewlett Packard GC with autosampler and mass selective detector) with mode of Selective Ion Monitoring (SIM) was used for determination of pesticides. $1\ \text{mL}\ \text{min}^{-1}$ of Helium was used as carrier gas, injector temperature was 275°C and the detector temperature was 300°C . Initial temperature 90°C was held for 3.0 min, ramped at $20^{\circ}\text{C}\ \text{min}^{-1}$ and then final temperature 280°C was held at 3.0 min (El-Shenawy *et al.*, 2009).

The Mean Accumulation Factors (MAF) were calculated for both the receiving phase and each diffusion-limiting membrane material. This accumulation factor gives a measurement of the uptake rate of the device fitted with different diffusion-limiting membranes related to the concentration of each analyte to which it is exposed and was calculated as follows:

$$\text{Accumulation factor (MAF)} = C_d/C_w$$

where, C_d is concentration accumulated in the C_{18} receiving phase following exposure time in units of ng disk^{-1} . The C_w is average concentration in the exposure tank during deployment in units of ng mL^{-1} .

Ecoscope Passive Sampler

It was provided by Km Labs, Sweden (Fig. 2B). This device is designed to be suitable for detection of organic micro pollutants by means of accumulation in a hexane receiving-phase. The system consists of hexane-filled bag made of dialysis membrane, held within a protective plastic housing. The Ecoscope samplers were provided pre-loaded with the hexane receiving-phase. The sampler were transported and stored refrigerated in sealed polyethylene bottles containing distilled water until the deployment in the field. The samples were fully submerged throughout deployment. At the end of the deployment time, the Ecoscope samplers were pulled apart two halves to reveal the dialysis bag containing the hexane to detect the pollutants (diuron and irgarol). The contents of the bag emptied into graduated glass test-tube and the volume of hexane was recorded. The 1 mL aliquot of hexane was placed in another test tube and 25 μL of the internal standard ^{10}D -phenanthrene ($1 \text{ ng } \mu\text{L}^{-1}$) in 2, 2, 4-trimethylpentane added. The volume of the solution was reduced to 250 μL and placed in a 250 μL insert of the autosampler vial in preparation for analysis by GC-MS.

Mussels Samples

Specimens of *M. edulis* were collected from South Parade Pier and transported to the marine laboratory (Fig. 1D). Live organisms were transported to the laboratory where they were held for a few days in aerated artificial seawater to settle down and eliminate possible contamination. Some individuals were placed in mesh bag then used as the control sample and deployed in reference site and some others were deployed at the two sites of monitored water for the whole exposure period (14 days). Each bag contained 21 mussels, where they were deployed alongside the passive samplers at each site. Part of exposed mussels was collected after 7 and 14 days of exposure, respectively. At the end of deployment time, the mussel whole soft tissues except the stomach were dissected out and homogenized with anhydrous sodium sulphate. Each mussel sample consisted of 3 individual. The accumulation of the organic compounds in mussels tissues were analyzed using the method of El-Shenawy *et al.* (2007). A GC/MSD method for quantifying the pollutants has been developed. The method is based on extraction with acetone-hexane (100 mL 2:3, v/v), followed by adsorption column chromatography cleanup on florisil columns and their subsequent determination using gas chromatography with mass selective detection (GC-MSD).

Water Samples

Techniques have been established for the quantitative isolation of the test compounds from aqueous media by means of liquid-liquid extraction and their subsequent determination using GC-MSD. One liter of seawater was mixed with 20 mL of dichloromethane (HPLC grade) in a separation funnel. The mixture was shaken vigorously for 2 min and then phases were allowed to separate. The aqueous phase was extracted twice more with 20 and 10 mL aliquots of dichloromethane (HPLC grade). Solvent extracts were combined and allowed to pass through an anhydrous sodium sulphate column pre-washed with dichloromethane to remove any residual water. The volume of the solvent was reduced by blowing down in a gentle stream of nitrogen gas. The sample was re-dissolved in 5 mL of iso-octane:ethyl acetate (50:50) and spiked with 100 μL of an internal standard (^{10}d -phenanthrene) ($1 \text{ ng } \mu\text{L}^{-1}$). The

sample was then concentrated under a stream of nitrogen gas to a volume of exactly 1 mL. The final extract was transferred to a 2 mL autosampler vial and 2 μ L of the extract was injected under the chromatographic conditions as described above and components detected selective ion monitoring (Vrana *et al.*, 2005b).

Deployment of Samples

In order to carry out this study, the two types of passive sampler; Chemcatcher (n = 6) and Ecoscope (n = 6) and biomonitoring mussels (2 mesh bags each contains 21 individual) were deployed at each of the chosen sites (Haslar, Port Solent marinas and Portsmouth raft site in Langston Harbour, Portsmouth) (Fig. 1A-1C) for a period of 7 and 14 days. The accumulations of organic pollutants within each sample and within the tissue of mussels were determined at the end of each deployment period. In tandem with this study, samples of water were taken regularly from each site and the concentrations of a range of organic micro pollutants within each sample were determined. During this field samples were deployed for a period of one and two weeks at each site. It was therefore necessary to visit the site only when the samplers were initially deployed and when they were collected for final analysis. In contrast the taking of such regular 1 L spot samples, 10 samples in 14 days, required regular visits to the deployment sites. The samplers remained *in situ* for 1 week after which 3 samplers from each site were removed for analysis. The trial continued for a further week after which the remaining 3 samplers were removed. The accumulation of eight organic pollutants in the receiving phase of the passive sampler was determined by solvent extraction followed by analysis by GC-MS.

RESULTS

Spot Sampling

Typical percentage recoveries for each of the compounds contained in the test set are shown in Table 1. The aqueous concentration of diuron, irgarol, atrazine and phenanthrene of the two deployment sites (Haslar marina and Port Solent) during field trial are shown in Table 2 and 3. The concentrations at each site fluctuated throughout the study (Fig. 3, 4). At the Haslar marina the concentration of diuron fluctuated between

Table 1: Typical percentage recoveries for each of the compounds used in the field

| Compounds | Recovery (%) ^a |
|---------------|---------------------------|
| Atrazine | 106.7 \pm 4.0 |
| Diuron | 104.2 \pm 5.6 |
| γ -HCH | |
| Irgarol | (not detected) |
| Phenanthrene | 99.2 \pm 3.4 |
| Dieldrin | 99.7 \pm 5.6 |
| PCB 52 | 98.0 \pm 4.1 |
| PCB 153 | 82.5 \pm 5.9 |

^aMean \pm SD of each organic analyte extracted from aqueous media and analyzed using GC-MSD (No. of replicates = 10)

Table 2: The mean concentrations of the diuron, irgarol, atrazine and phenanthrene in water samples (1 L) from Haslar marina, Gosport, Portsmouth UK during the deployment of the mussels and passive samplers for 14 days in the field

| Pesticides | Concentration (ng L ⁻¹) of the first week ^a | Concentration (ng L ⁻¹) of second week ^a | Concentration (ng L ⁻¹) after 14 days deployment ^a |
|--------------|--|---|---|
| Diuron | 31.4 \pm 2.6 | 71.0 \pm 10 ^b | 51.2 \pm 8.2 |
| Irgarol | 3.0 \pm 0.1 | 5.3 \pm 0.4 ^b | 4.2 \pm 0.4 |
| Atrazine | 3.1 \pm 0.4 | 3.6 \pm 0.1 | 3.3 \pm 0.2 |
| Phenanthrene | 4.7 \pm 0.9 | 4.5 \pm 1.0 | 4.6 \pm 0.6 |

^aMean \pm SE of the water concentrations of organic analytes after 14 days deployment of the passive sampler and mussel.

^bSignificant difference as compared to the first week (Student t-test, p<0.05)

Table 3: The mean concentrations of the diuron, irgarol, atrazine and phenanthrene in water samples (1 L) from Port Solent Marina, Portsmouth UK during the deployment of the mussels and passive samplers for 14 days in the field

| Pesticides | Concentration (ng L ⁻¹) of the first week ^a | Concentration (ng L ⁻¹) of second week ^a | Concentration (ng L ⁻¹) after 14 days deployment ^a |
|--------------|--|---|---|
| Diuron | 2035.0±199 | 3106.0±458.0 ^b | 2753.5±323.8 |
| Irgarol | 278.0±18.4 | 297.0±36.0 ^b | 292.6±18.0 |
| Atrazine | 14.4±1.9 | 21.0±3.4 ^b | 17.7±2.0 |
| Phenanthrene | 15.2±10.4 | 13.8±3.2 | 14.4±4.0 |

^aMean±SE of the water concentrations of organic analytes after 14 days deployment of the passive samples and mussel.

^bSignificant difference as compared to the first week (Student t-test, p<0.05)

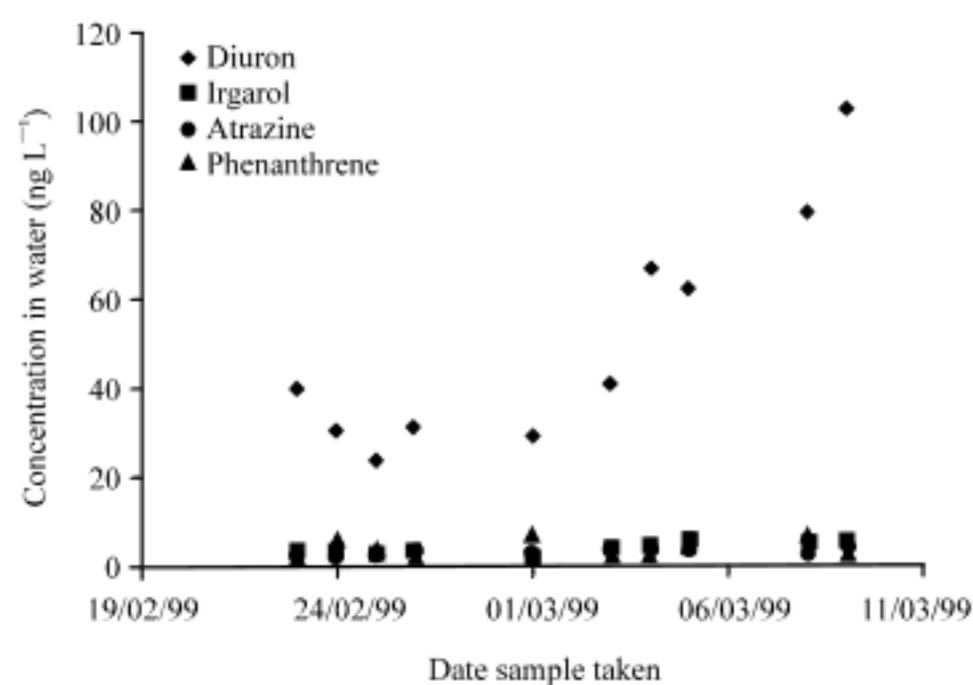


Fig. 3: The aqueous concentrations of diuron, irgarol, atrazine and phenanthrene in 1 L spot samples taken from Haslar marina during deployment of the passive samplers and mussels

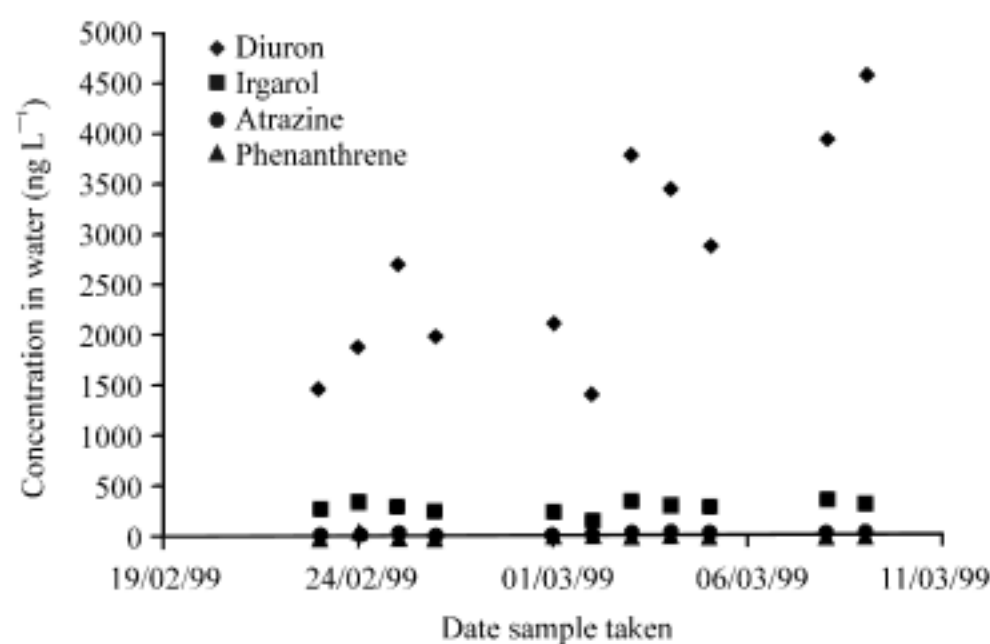


Fig. 4: The aqueous concentrations of diuron, irgarol, atrazine and phenanthrene in 1 L spot samples taken from Port Solent marina during deployment of passive samplers and mussels

24.1 and 103.2 ng L⁻¹ with a mean of 51.2 ng L⁻¹ and the irgarol 1051 concentration fluctuated from 2.7 to 6.1 ng L⁻¹ with a mean of 4.2 ng L⁻¹. Atrazine concentration fluctuated from 2.2 to 4.1 ng L⁻¹ with a mean of 3.3 ng L⁻¹. Phenanthrene concentration fluctuated from 2.5 to 7.9 ng L⁻¹ with a mean of 4.6 ng L⁻¹.

The average water concentrations of diuron during the first week were 31.4 ng L⁻¹ at the Haslar marina and 2035.0 ng L⁻¹ at Port Solent marina as opposed to a mean of 71.0 and 3106.0 ng L⁻¹, respectively during the second week (Table 2, 3). Similar changes in aqueous concentration of irgarol, atrazine and phenanthrene were seen over the same sampling period (Table 2). The diuron concentration which detected every day for 14 days at Port Solent varied from 1422 and 4584 ng L⁻¹ with a mean of 2753.5 ng L⁻¹ and the irgarol 1051 concentration fluctuated from 166 to 369 ng L⁻¹ with a mean of 292.6 ng L⁻¹. Atrazine levels fluctuated from 7.6 ng L to 24.6 ng L⁻¹ with a mean of 17.7 ng L⁻¹ and the range of concentrations of phenanthrene was 2.2 to 25.6 ng L⁻¹ with a mean of 14.4 ng L⁻¹.

In general the concentrations of both diuron and irgarol 1051 were a factor of between 50-70 higher at the more enclosed Port Solent site. Also, there was a marked rise in aqueous concentration of both analytes during the second week of the sampling compared with the first week. None of the samples taken during the survey from the reference site in Langstone Harbour contained diuron or irgarol at detectable levels.

Accumulation of Organic Pollutants by Passive Samplers **Chemcatcher Passive Sampler**

The performance of the sampler was tested by exposure to constant concentrations of test chemicals in a continuous flow exposure tank. Concentrations of the analytes in water (CW) and the amounts accumulated in the receiving disk (mD) were two parameters measured regularly during the continuous flow-exposures. During exposure the water concentration was held constant and this was confirmed by analyses of water samples. Satisfactory linear regression fits of the equation to the uptake data of analytes from water to the sampler discs were obtained for all test compounds in all experiments.

Table 4 shows the mass of each analyte accumulated in the C₁₈ receiving phase of the passive sampling device following deployments of 7 and 14 days. As long as equilibrium is not approached this uptake will be linear with time for the duration of deployment. The passive sampling device results for all the organic pollutant show a low standard error in the mass accumulated. This is precise in comparison to the fluctuations in analyte concentration measured using spot samples throughout the same period which show a higher standard error.

The diffusion-limiting membrane although, slightly discoloured appeared to be free from bacterial and algal fouling and the downwards vertical orientation of the device resulted in minimal silting of the membrane surface. This orientation of the passive samples during deployment is vital as it is anticipated that fouling of the unprotected membrane surface may

Table 4: Accumulation of organic analytes by Chemcatcher passive sampler (ng device⁻¹) from Haslar and Port Solent Marina during the deployment period (14 days)

| Organic analytes | Area of investigation | | | |
|------------------|------------------------|------------------------|------------------------|--------------------------|
| | Haslar Marina | | Port Solent Marina | |
| | Duration of deployment | | Duration of deployment | |
| | 7 (days) ^a | 14 (days) ^a | 7 (days) ^a | 14 (days) ^a |
| Diuron | 6.6±0.5 | 17.3±1.3 ^b | 417.8±8.6 | 1500.0±11.8 ^b |
| Atrazine | 3.7±0.6 | 5.9±1.4 ^b | 5.2±0.7 | 6.000±0.4 |
| Lindane | 3.0±0.6 | 3.2±0.5 | 0.8±0.3 | - ^c |
| Phenanthrene | 11.7±0.4 | 7.4±0.7 ^b | 10.7±0.8 | 8.200±0.7 |
| PCB 153 | 4.6±3.0 | 2.8±1.6 ^b | 2.0±0.5 | 1.700±0.3 |
| PCB 52 | 2.7±1.2 | 5.3±2.6 ^b | 1.9±0.4 | - ^c |
| Irgarol | - ^c | - ^c | 43.4±1.0 | 125.00±0.3 ^b |

^aMean±SE of the accumulation of organic pollutant by Chemcatcher passive sampler (n = 3). ^bSignificant difference as compared to the first week (Student t-test, p<0.05). ^c - Not detected

Table 5: Accumulation (ng L⁻¹) of diuron, irgarol and phenanthrene in the Ecoscope passive sampler deployed at Haslar and Port Solent Marina

| Organic analytes | Area of investigation | | | |
|------------------|------------------------|------------------------|------------------------|------------------------|
| | Haslar Marina | | Port Solent Marina | |
| | Duration of deployment | | Duration of deployment | |
| | 7 (days) ^a | 14 (days) ^a | 7 (days) ^a | 14 (days) ^a |
| Diuron | - | - | 1.4±0.1 | 1.5±0.1 |
| Phenanthrene | 2.3±0.1 | 3.7±0.1 | 3.9±0.3 | 9.1±0.3 ^b |
| Irgarol | 0.3±0.1 | - | 11.2±1.1 | 22.4±6.2 ^b |

^aMean±SE of the organic pollutants. ^bSignificant difference as compared to the first week (Student t-test, p<0.05). - Not detected

result in a decrease in the rate of diffusion of the organic determine and through the diffusion limiting membrane. Significant fouling of the membrane surface, either by means of the formation of a biofilm or by simple silting of the membrane, would render invalid the calibrations carried out in separate laboratory studies. Accurate information on the time averaged concentrations of the analytes would be lost and the accumulation data would at best give semi-quantitative information. After 14 days of deployment, the concentrations of diuron and irgarol were 1500.0±11.8 and 125.0±0.3 ng device⁻¹ in port Solent marina as compared to 17.3±1.3 ng device⁻¹ and not detected in Haslar marina, respectively. As expected, the samplers deployed at the reference site in Langatone harbour contained no diuron or irgarol 1051 at detectable levels.

Ecoscope Passive Sampler

Table 5 shows the accumulation of organic pollutants within hexane receiving phase of the Ecoscope passive samplers deployed at Haslar marina and Port Solent site for 2 weeks. The mass of the three analytes accumulated by the Ecoscope samplers is far lower than that accumulated within the C₁₈ receiving phase of the Chemcatcher passive sampler. This is particularly so in the case of the herbicide diuron which, despite aqueous concentrations at the Port Solent site during deployment of the levels between 1422 and 4584 ng L⁻¹, was not found in the hexane of the Ecoscopes exposed during this period. This compares with a mean of 1500 ng device⁻¹ accumulated within the receiving phase of the Chemcatcher sampler under the same conditions of exposure. Igarol 1051 was present in lower concentrations at both exposure sites but was not detected at Haslar Marina even after 2 weeks exposure. However, at port Solent, where the average aqueous concentration of irgarol 1051 during the 2-week deployment period was 293 ng L⁻¹, the Ecoscope samplers accumulated an average of 22.4 ng L⁻¹. This again can compared with a higher mass of 125 ng of irgarol 1051 accumulated in the C₁₈ receiving phase of the Chemcatcher passive sampler.

Accumulation of Organic Pollutants Within the Tissues of the Marine Mussel, *Mytilus edulis*

Table 6 summarizes the accumulation of the set of organic pollutants within the tissue of the mussels (ng g⁻¹ wet weight) deployed in Haslar and port Solent marinas for 14 days. Phenanthrene was accumulated to a very high concentration after one week of exposure in the Haslar marina but there was no significant difference between the concentration of phenanthrene in the mussels after one week and 2 weeks (99.4±9.0 and 78.2±9.1 ng g⁻¹ wet weight¹, respectively). Similar results were obtained in the port Solent marina where the concentration of phenanthrene in mussel tissues was 107.0±11.0 ng g⁻¹ wet weight¹ after one week of deployment compared with 103.0±10.0 ng g⁻¹ wet weight¹ after 2 weeks. This may indicate that the non-polar analytes rapidly reach steady state levels. Diuron was found to

Table 6: Accumulation (ng g⁻¹ wet weight) of organic analytes by mussels exposed in the Haslar and the Port Solent Marina for 7 and 14 days

| Organic analytes | Area of investigation | | | |
|------------------|------------------------|------------------------|------------------------|------------------------|
| | Haslar Marina | | Port Solent Marina | |
| | Duration of deployment | | Duration of deployment | |
| | 7 (days) ^a | 14 (days) ^a | 7 (days) ^a | 14 (days) ^a |
| Diuron | 0.7±0.1 | 0.78±0.1 | 12.2±2.4 | 14.0±1.7 |
| Atrazine | 24.3±8.4 | 18.5±7.8 | 15.3±6.0 | 21.3±8.4 |
| Lindane | 64.8±19.0 | 36.7±4.8 b | 46.8±12.3 | 35.0±3.6 |
| Phenanthrene | 99.4±9.0 | 78.2±9.1 b | 107.0±11.0 | 103.0±10.0 |
| PCB 52 | 7.2±0.7 | 8.7±1.4 | 8.7±1.3 | 9.5±1.6 |
| Irgarol | 2.3±0.9 | 6.4±1.5 b | 20.0±5.0 | 13.5±2.9 b |
| PCB 153 | 4.2±0.3 | 4.4±0.8 | 4.2±0.7 | 3.8±0.4 |

^aMean±SE of the pollutant concentration in mussel tissues (n = 6, each sample consists of 3 animals). ^bSignificant difference as compared to the first week (Student t-test, p<0.05)

Table 7: Accumulation (µg/lipid content of 50 mg dry tissue) of organic analytes by mussels exposed in the Haslar and the Port Solent Marina for 7 and 14 days

| Organic analytes | Area of investigation | | | |
|------------------|------------------------|------------------------|------------------------|------------------------|
| | Haslar Marina | | Port Solent Marina | |
| | Duration of deployment | | Duration of deployment | |
| | 7 (days) ^a | 14 (days) ^a | 7 (days) ^a | 14 (days) ^a |
| Diuron | 1.5±0.3 | 1.9±0.2 | 16.6±2.7 | 21.0±0.6 |
| Atrazine | 47.4±13.0 | 43.3±20.0 | 21.6±8.3 | 29.5±8.2 |
| Lindane | 125.2±26.0 | 87.1±7.8 b | 67.8±2.4 | 54.3±5.4 |
| Phenanthrene | 201.0±14.0 | 183.5±9.9 b | 150.2±2.4 | 157.4±7.2 |
| PCB 52 | 14.8±1.7 | 20.3±2.0 b | 11.8±1.6 | 14.0±0.5 |
| Irgarol | 4.5±1.7 | 15.2±4.0 b | 29.2±8.4 | 19.2±2.0 b |
| PCB 153 | 8.5±0.5 | 10.2±1.2 | 6.1±1.0 | 6.0±0.6 |

^aMean±SE of the pollutant concentration in mussel tissues (n = 6, each sample consists of 3 animals). ^bSignificant difference as compared to the first week (Student t-test, p<0.05)

accumulate in the tissues of the mussels and there was little variation between samples compared with some of the other analytes. At port Solent marina the mean concentration of Diuron after two weeks was 14.0±1.7 ng g⁻¹ wet weight (Table 6). Table 7 shows the accumulation of the pollutant in mussels tissue expressed as µg/lipid tent of 50 mg dry tissue. The entire mentioned compounds above did not detect in the tissue of mussels that deployment in Langatone harbour at detectable levels.

DISCUSSION

The time averaged concentrations of organic pollutants over a two week period at the two marina sites and the reference site in Langstone Harbour were measured using three different techniques. Values obtained by means of passive sampling tend to be lower than obtained by spot sampling. This may be due to these sites were quite sheltered and as such the turbulence of the water may have been considerably less than that of the water in the exposure tank where the calibrations of the device were carried out (Kingston *et al.*, 2000; Vrana *et al.*, 2005b; El-Shenawy *et al.*, 2009). However, the result in this study indicated that either technique can give an adequate reflection of the concentrations of organic pollutants over time.

Fouling of the diffusion-limiting membrane surface may, in part, account for the low accumulation of the two compounds by the Ecoscope passive samples at Haslar marina. However, as aqueous concentrations at port Solent of diuron were between 1422 and 4584 ng L⁻¹ and of irgarol 1051 were between 166 and 369 ng L⁻¹ a higher accumulation may have been expected and therefore an alternative explanation must be sought. The partitioning of organic compounds from the aquatic environment into the receiving phase of a passive sampling device is a process controlled by two major factors (Sabaliunas and Sodergren, 1996). Firstly, the permeability of the diffusion-limiting membrane and its affinity for the analytes of interest since these control the speed of diffusion of a dissolved species through the membrane and the length of any lag phase before significant accumulation may be observed. Secondly, the affinity of the receiving phase for a particular analyte drives the process. The analyte of interest must have a far greater affinity for the receiving phase of the passive sampling system than for water phase in order to maintain a concentration of zero at the surface of the receiving phase. Under these circumstances the rate of accumulation is dependent on the environmental concentration. These two factors combined to produce a sampling rate for a particular system/analyte combination that can be determined in separate laboratory tank studies (El-Shenawy *et al.*, 2009).

In the case of the two compounds diuron and irgarol 1051 the low sampling rates of the Ecoscope passive samplers observed in the field trial (Table 4) may be due to the properties of the dialysis membrane, the receiving phase or a combination of both. One explanation of this phenomenon is simply that the pores of the dialysis membrane are too small to allow rapid diffusion, resulting in a low flux of compounds, dissolved in the aqueous environment, through the membrane into the hexane receiving phase of the Ecoscope passive sampler. However, this is unlikely as the dialysis membrane used has molecular weight cutoff of 3500 and therefore should not hinder the diffusion of these relatively small molecules with molecular weight of 253 for irgarol and 248 for diuron. An alternative explanation lies in the physico-chemical properties of the two target analytes. Diuron and irgarol are relatively polar (having log octanol water partition coefficients of 2.80 and 3.95, respectively) in comparison with the non-polar compounds such as organochlorine pesticides and PCBs that have been reported to be detected in previously published data using similar hexane-filled dialysis bag systems (Sodergren, 1990; Johnson, 1991). It can be hypothesized that the partitioning of these relatively polar compounds (diuron in particular) from water into the hexane receiving phase of the Ecoscope may be thermodynamically less favorable than their partitioning into the C₁₈ phase of the Chemcatcher sampler under identical conditions. This would explain the lower than expected accumulation of these particular organic compounds in the Ecoscope relative to that in the Chemcatcher sampler. The equilibrium partition values of irgarol between water and hexane is unavailable at present. However, the hexane-water log P value of diuron is quoted in the Med-chem database as -0.21. This negative log-partition coefficient explains the low uptake of diuron within the hexane receiving phase of the Ecoscope passive sampler. It would be interesting to investigate further the behaviour of the Ecoscope samplers with a wider range of analytes and this could form part of future studies in this area.

The efficacy of passive sampling for determining the distribution and concentration of organic micro pollutants in the aquatic environment has been compared in a number of laboratory and field surveys with that of biomonitoring (Sodergren, 1990; Herve *et al.*, 1991; Ellis *et al.*, 1995; Peven *et al.*, 1996; Hofelt and Shea, 1997). The uptake of the diuron and irgarol in the tissues of the mussels was low in comparison with that observed with the Chemcatcher sampler. This can be related to the physicochemical properties of the two

compounds. The rate and extent of the bioaccumulation of particular organic compounds within the lipid tissues of aquatic organisms has been related to the lipophilicity of that compound (Gobas and Mackay, 1987). Both these compounds (irgarol and duiron) have log P value less than 4 and are therefore not classified as lipophilic compounds under criteria described by Noble (1993). Duiro is more polar analyte with a log P value of 2.80 compared with a log p value of 3.85 for irgarol. It is therefore expected that the bioaccumulation of irgarol 1051 would be more rapid than that of diuron. This can indeed be observed from the data obtained during the field trial. The mass of diuron accumulated within the tissues of the biomonitoring organism was generally equal or less than irgarol 1051 despite the significantly greater concentration of diuron found at each site by means of spot sampling. In the Haslar marina there was no significant increase in the bioaccumulation of lindane, PCB 52 and phenanthrene in the tissues of the mussels when the time of the deployment was extend from one to two weeks.

In this study, bioaccumulation of some analytes (phenenthrene and lindane) was far greater than uptake by passive samples and this may reflect the far greater surface area to volume ratio of the living organisms, the force flow of the water over the permeable respiratory surface and the enhancement of capacity over that n-hexane by dense lipids and possibly protein binding. Further, the mussels may have acquired some of their body burden of pollutants from their food. The enhanced capacity due to biological lipids and proteins may explain the discrepancies between the lipids normalized concentrations observed in *M. edulis* and triolein-filled passive samplers by Hofelt and Shea (1997). Sodergren (1990) found a 5000-fold increase in accumulation of low-chlorinated PCBs by *Gammarus pulex* over n-hexane filled samplers and Herve *et al.* (1991) found a similar pattern with these samplers and freshwater mussels. On a lipid normalized basis the concentrations of all organochlorines in the study of Prest *et al.* (1992) were 10 to 100 times higher in freshwater clams than in triolein-filled samplers. These discrepancies reflected the non-equilibrium status of their samplers in which more than a year was predicted to be necessary to achieve equilibrium for high molecular weight analytes. However, caution has been recommended when comparing organisms and semipermeable membrane devices (SPMDs) on a lipid normalized basis since a key assumption is that the levels of analyte within an organism have reached steady state (Prest *et al.*, 1992, 1995). Where humic materials (in the form of aggregates, colloids and micelles) are present they may reflect the availability of materials such as PAHs and certain organochlorine compounds (e.g., DDT) which bind strongly to those components. Under these circumstances uptake by particulate feeding organisms would be expected to be far greater than that by passive samplers (Herve *et al.*, 1991). In general the accumulation in individuals exposed for one week was greater than in those exposed for two weeks and this may be due to metabolism or exupuration.

CONCLUSION

Passive sampling devices and biomonitoring organisms may provide complementary information since, the former samples only the free fraction and the latter both the free and particulate-bound fractions of pollutants in aquatic environments. The utility of the passive systems can be further extended by linking them to toxicological assays. The Chemcatcher samples has been useful to overcome some of the deficiencies of existing devices and to cover a wide range of polarities.

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