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RESEARCH ARTICLE

Passive sampling of selected pesticides in aquatic environment using polar organic chemical integrative samplers

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Abstract
Purpose Polar chemical integrative samplers (POCIS) were examined for their sampling efficiency of 12 pesticides and one metabolite commonly detected in surface waters. Laboratory-based calibration experiments of POCISs were conducted. The determined passive sampling rates were applied for the monitoring of pesticides levels in Lake Amvrakia, Western Greece. Spot sampling was also performed for comparison purposes.
Methods Calibration experiments were performed on the basis of static renewal exposure of POCIS under stirred conditions for different time periods of up to 28 days. The analytical procedures were based on the coupling of POCIS and solid phase extraction by Oasis HLB cartridges with gas chromatography–mass spectrometry.
Results The recovery of the target pesticides from the POCIS was generally >79% with relative standard deviation (RSD) <16%. The calibration results revealed an integrative uptake of all pesticides for 28 days and the calculated sampling rates ranged from 0.025 to 0.388 L day^{-1} with RSD <29%. Low nanogram/liter levels of pesticides such as diazinon, alachlor, and *s*-metolachlor were detected during the monitoring campaign using both passive and spot sampling whereas higher concentrations were measured by spot sampling in most cases.
Conclusions Passive sampling by POCIS provides a useful tool for the monitoring of pesticides in aquatic systems since integrative sampling at rates sufficient for analytical quantitation of ambient levels was observed. Calibration data are in demand for a greater number of compounds in order to extend the use in environmental monitoring.

Keywords Passive sampling · POCIS · Pesticides · Monitoring · Waters · GC–MS

1 Introduction

Pesticides enter surface waters mainly through surface run-off and also through sewage plant outlets and sewer overflows, through accidental spills, and to a much lesser extent through aerial drift and precipitation from the atmosphere, resulting in high spatio-temporal variability of their concentrations in surface waters. The characterization of the spatio-temporal variability and episodic events of pesticide inputs and the risk associated with their levels requires extensive water monitoring programs, designed according to the relevant scales and dissipation processes, that are costly and time consuming (Konstantinou et al. 2008).

Routine water monitoring mainly relies on spot (grab) sampling at fixed intervals. The analysis of spot samples provides only an instantaneous estimate of the pollutant's concentration at the time and point of sampling and is likely to miss peak inputs in a given aquatic system or the presence of contaminants at trace levels. In recent years, time-integrative passive sampling methods have been developed to complement and/or replace spot sampling

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methods. Similarly to biomonitoring techniques, time-integrative passive sampling enables the determination of time-weighted average (TWA) concentration of the dissolved phase over extended sampling periods, which is a fundamental part of an ecological risk assessment process for aquatic contaminants. In addition, passive sampling enables the preconcentration of contaminants, increasing the capability for detecting trace concentrations that otherwise requires the extraction of several liters of water (Martinez-Bueno et al. 2009). The use of passive accumulation devices (PADs) in the regular monitoring of chemicals can be applied for the surveillance or operational and investigative monitoring that is necessary to meet the requirements of the Water Framework Directive (Stuer-Lauridsen 2005).

The principle of operation of passive sampling in water has been described previously (Goreki and Namiesnik 2002; Vrana et al. 2005; Booij et al. 2007; Alvarez et al. 2004, 2007). Generally, passive sampling techniques are based on the diffusion of chemicals from a medium to a receiving phase that is separated from the medium by a membrane, basically due to a difference in the chemical potential gradients. The uptake of the analytes depends on several factors such as the properties of both the receiving phase and the membrane, the physicochemical properties of the compounds, and environmental parameters such as temperature, water properties (pH, salinity, etc.), water turbulence and flow, biofouling of the membrane, etc. (Vrana et al. 2005; Söderström et al. 2009).

Throughout the last decade, aquatic passive sampling has received increasing attention and a growing number of devices have been presented in the literature, such as semipermeable membrane device (Huckins et al. 1993), the polar organic chemical integrative samplers (POCIS) (Alvarez et al. 2004), Chemcatcher® (Vrana et al. 2006a), diffusive gradients in thin films (Allan et al. 2007), and membrane-enclosed sorptive coating (Vrana et al. 2006b), and they have been used for the monitoring of various pollutants in surface waters. Among them, the POCIS and Chemcatcher® samplers have been applied successfully for the screening and the determination of TWA concentrations of polar organic micropollutants including pesticides (Schafer et al. 2008; Alvarez et al. 2005, 2007; Escher et al. 2006; Arditsoglou and Voutsa 2008) in various aquatic environments (wastewater effluents, streams, lakes, rivers, and coastal waters).

For the estimation of water concentration of pesticides, calibration data (sampling rates) of the passive samplers are necessary. Limited data are available on sampling rates of pesticide compounds under various conditions (Alvarez et al. 2007; Mazzella et al. 2007; Martinez-Bueno et al. 2009). The capability of PADs for detecting trace concentrations of contaminants in water remains to be tested for a wide range of compounds including pesticides and in various aquatic systems.

The aims of this study were: (a) to determine the sampling rates of the target pesticides using POCIS based on laboratory calibration experiments and (b) to evaluate the applicability of POCIS for TWA concentration measurements during a field study in Lake Amvrakia. There is a lack of data on the sampling efficiency and sampling rates using pest-POCIS for most of the pesticides studied according to the best of our knowledge. Complementary data on the sampling rates of some previously studied pesticides such as atrazine, simazine, diazinon, and malathion are also reported herein for comparison purposes. The pesticide compounds (atrazine, atrazine-deethyl, simazine, prometryne, alachlor, *s*-metolachlor, chlorpyrifos, chlorpyrifos methyl, diazinon, malathion, benalaxyl, pyrimethanil, triadimenol) were chosen on the basis of 1-year monitoring in the sampling region and of their frequent detection in surface waters of agricultural areas of Greece and other European countries (Konstantinou et al. 2006) while most of them are considered as priority pollutants.

2 Experimental section

2.1 Chemicals, standards, and materials

The pesticide standards atrazine, atrazine desethyl, simazine, prometryne, diazinon, pyrimethanil, chlorpyrifos methyl, alachlor, malathion, *s*-metolachlor, chlorpyrifos, triadimenol, benalaxyl, and pirimiphos methyl were purchased at analytical grade (>97.3% purity) from Sigma-Aldrich (Steinheim, Germany). Methanol and *n*-hexane were supplied from Pestiscan (Dublin, Ireland). Dichloromethane and ethyl acetate were supplied from Roth (Karlsruhe, Germany), and toluene was supplied from Riedel de Haën (Seelze, Germany). Individual stock standard solutions were prepared in methanol and stored in amber glass vials at −18°C. Commercial cartridges packed with Oasis™ HLB (divinylbenzene/*N*-vinylpyrrolidone copolymer, 200 mg, 6 cm^3) were purchased from Waters (Mildford, MA, USA). The POCIS (47 mm i.d. membrane disks) were provided by Exposmeter SA (Tavelsjö, Sweden) with the "generic" configuration for pesticide sampling (pest-POCIS). The samplers contained 200 mg of a triphasic sorbent admixture: hydroxylated polystyrene-divinylbenzene resin (Isolute ENV+) /carbonaceous sorbent (Ambersorb 572), 80:20 (*w*/*w*), dispersed on styrene-divinylbenzene copolymer (S-X3 Bio Beads) and was enclosed between two hydrophilic polyethersulfone (PES) microporous membranes (130 μm thickness, 0.1 μm pore size). Each POCIS unit had an effective sampling surface area of ~41 cm^2 and a membrane surface area to sorbent mass ratio of ~180 cm^2/g

as described by Alvarez et al. (2004). HVLP (0.45 μm) filters from Millipore (Bedford, MA, USA) were used for the filtration of water samples.

2.2 Calibration of POCIS

Prior to the deployment of the POCIS samplers for the monitoring study, a calibration study was carried out in order to predict the TWA water concentrations of pesticide from levels accumulated in the POCIS. To characterize the uptake of the target pesticides by the POCIS, a kinetic study was conducted and sampling rates (R_s, L/d) were determined. Calibration experiments were performed on the basis of static renewal exposure of POCIS to the target compounds under stirred conditions (480 rpm) at constant ambient temperature 22±1°C monitored with laboratory thermometers. POCIS were placed in glass beakers, each one containing 1 L of filtered lake water fortified with 500 ng of each compound, stirred by a magnetic stirrer, and exposed for 3, 7, 14, 21, and 28 days in triplicate. The water was renewed every day with freshly spiked water. The concentration of pesticides over a 24-h exposure period was checked using a fourth glass beaker that contained fortified lake water following the methodologies described below. The results show a relatively constant concentration (relative standard deviation (RSD)=0.4–12.4%) in the exposure beakers with maximal observed losses of 11.5%. A POCIS disk placed inside of a fifth glass beaker, which contained non-fortified lake water, was used as a background control blank (Alvarez et al. 2004) to assess contamination during the experiment. All beakers were covered with aluminum foil to reduce exposure to light and minimize the volatilization of the analytes. The sampling rate (R_s, L/d) for each target compound was calculated by the following equation:

$$R_s = \left(\frac{C_{POCIS} \times M_{POCIS}}{C_W \times t} \right) \quad (1)$$

where C_{POCIS} (ng/g) is the concentration of the analyte in the sorbent, M_{POCIS} (g) is the mass of the sorbent within the POCIS, C_w (ng/L) is the mean concentration of the analyte in water, and t is the sampling period (day). In the present study, Eq. 1 has been transformed in terms of a concentration factor, CF_t, as follows

$$CF_t = Ms_t / C_w = R_s t \quad (2)$$

where Ms_t is the mass of the analyte (ng) accumulated in the sampler at exposure time t. The plot of the concentration factor CF_t versus time is a linear curve until the sampler reaches half-saturation, the slope of which represents the sampling rate, R_s, of the analyte (Tran et al. 2007). Linear uptake models were fitted through origin.

2.3 Description of the area and sampling strategy

Lake Amvrakia is a deep, warm monomictic and sulfate lake in Western Greece. Its surface is 12 km^2 and the drainage basin amounts to 121 km^2. The surface area has been significantly reduced due to a prolonged drought and draining of the northern shallow part of the basin (Danielidis et al. 1996). The water level undergoes yearly fluctuations and depends on evaporation during summer, possible underground inlets, invisible discharges, and use of water for agricultural purposes (Danielidis et al. 1996). Mainly the east coast is intensively cultivated up to only a few meters away from the water edge and also serves as pasture land for sheep. During the deployment period, the average temperature in the lake ranged from 20°C to 27°C from May to July, respectively. Mean wind speed during the deployment period was 2.7 m/s (data from meteorological station near the lake region) so the mean wind-driven surface water currents can be estimated to be about 8 cm/s, assuming that the surface current in lakes is about 3% of the wind current (Goldman and Horne 1994). A map of the lake catchment area and the land uses are shown in Fig. 1.

The samplers, in air-tight metal cans, were stored in laboratory conditions and transported in portable refrigerators to the field. The POCIS disks were attached in stainless steel holders in situ and were placed in stainless steel canisters provided by Exposmeter SA (Tavelsjö, Sweden). The canisters were bounded to floating balls in a vertical position and at a depth of 2 to 3 m in the lake water column at the sampling sites A1 (lake depth 20 m), A2 (lake depth 35 m), and A3 (lake depth 30 m) which were selected according to agricultural land uses around Lake Amvrakia (located mainly in the east side of the lake; Fig. 1) and the hydrologic characteristics of the catchment (streams entering into the lake). The samplers were deployed twice for 28 days during the period May–June 2009. At the end of the exposure period, the POCIS were slightly or not biofouled and they were rinsed with lake water and ultrapure water to remove any debris and to clean the nuts and bolts, wrapped in aluminum foil, and stored in their original containers, then transported to the laboratory under cooled conditions (~4°C). The extraction of the target compounds was carried out usually on the same day; otherwise, POCIS were stored frozen and the extraction was performed within 48 h. One blank POCIS was exposed to open air during the deployment and retrieval of the POCIS and was transported and analyzed as the deployed POCIS. Procedural blank consisted of POCIS taken through the entire processing and analysis sequence.

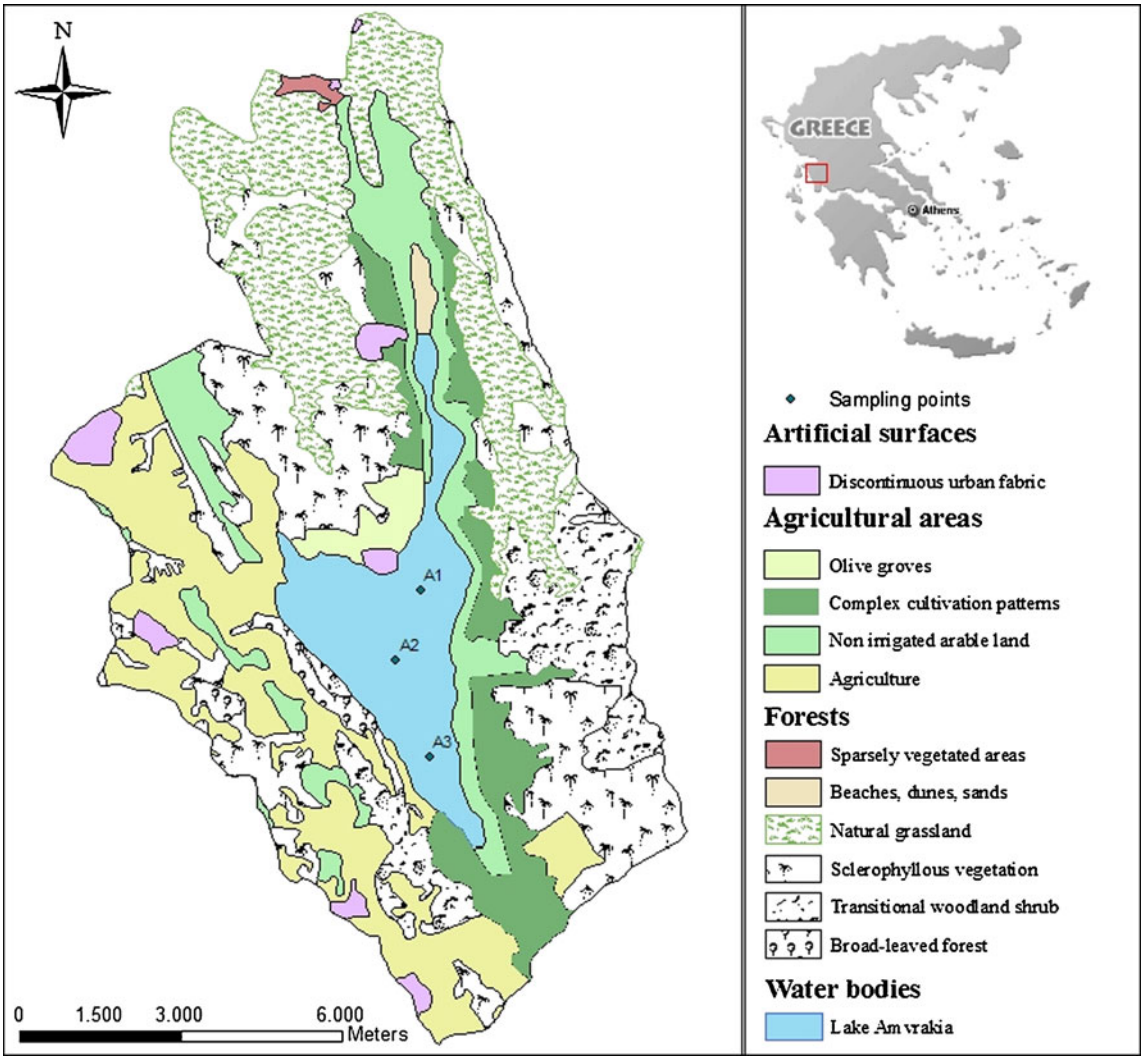

Fig. 1 Map of the study area (Lake Amvrakia), location of the sampling sites, and land uses of the catchment area

Spot sampling was also conducted. Water samples (1.5 L) were collected in pre-cleaned amber glass bottles from each sampling site twice, on the first and last day of the exposure period. Samples were acidified to pH 2.5 with sulfuric acid (1:1, *v*/*v*) to inhibit biological activity and stored at 4°C prior to extraction.

2.4 Extraction of pesticides from passive samplers and spot water samples

The loaded POCIS were disassembled carefully and the membranes were detached from the disk. The triphasic sequestration medium was transferred into a glass mortar and left at room temperature until dry. Then, it was weighed (200±46 mg, RSD=23%) and carefully transferred into empty solid phase extraction tubes (6 mL) packed between two polyethylene (PE) frits (20 μm porosity). SPE cartridges were disposed on a Visiprep SPE vacuum manifold (Supelco) and were eluted using 30 mL of a mixture of dichloromethane/methanol/toluene (8:1:1, *v*:*v*:*v*) (Alvarez et al. 2004). The eluate was reduced just to dryness in a gentle stream of nitrogen and the residue was dissolved in 0.5 mL of hexane for GC injections. For the recovery tests, the sorbent material was spiked with 100 μL of methanolic solution (3 μg L^{-1}) containing the studied pesticides, providing a spiking level of about 1.5 μg g^{-1}, in triplicate, dried at ambient temperature, and treated according to the above procedure.

The concentration of the target pesticides in lake water samples were determined using the calculated POCIS uptake rates, the concentrations quantified in the POCIS extract by GC–MS, the sampling time, and the mass of the sorbent extracted according to the following equation:

$$C_w = \frac{C_s M_s}{R_s t} \quad (3)$$

The procedural blank and the field blank yielded zero background contamination; therefore, they were not considered in Eq. 3.

The collected spot water samples (500 mL) were filtered through HVLP filters to eliminate particulate matter and extracted via SPE. Prior to the SPE, the Oasis HLB cartridges were washed with 10 mL of dichloromethane under vacuum followed by 10 mL of methanol and 10 mL of Milli-Q water. The water samples were allowed to percolate through the cartridges at a flow rate of 6 mL min^{-1} using a Visiprep SPE manifold (Supelco, Bellefonte, PA, USA). After sample extraction, the pesticides trapped in the cartridge were collected by using 5 mL of ethyl acetate—methanol (1:1, *v*/*v*) and 5 mL of ethyl acetate as eluting solvent. The fractions were evaporated just to dryness in a gentle stream of nitrogen and the residue was dissolved in 0.1 mL of hexane for GC injections. Pirimiphos methyl at 0.5 μg mL^{-1} was added as internal standard in both POCIS and SPE extracts.

2.5 Chromatographic analysis

A GC–MS QP 2010 Shimadzu instrument equipped with capillary column SLB-5MS (5% phenyl polysiloxane) 30× 0.25 mm×0.25 μm (Supelco, Bellefonte, PA, USA) was used under the following chromatographic conditions: injector temperature 220°C, column program of temperatures 50°C (1 min), 50–180°C (20°C/min), 180–190°C (10°C/min), 190–240°C (3°C/min), 240–300°C (10°C/min), 300°C (5 min). Helium was used as the carrier gas at 101.3 kPa and at a flow rate of 1.71 mL/min. The ion source and transfer were kept at 200°C and 280°C, respectively. A volume of 1 μL was injected in splitless mode. Three ions for each pesticide were chosen for screening analysis and, among these, the most abundant ion in the mass spectrum was used for quantitative analysis, in selected ion monitoring mode. The selection of the ions was based on high relative abundance and high value *m*/*z* of fragment ions from the mass spectrum while with the correct relative ion intensity (±20%).

2.6 Quality control, validation, and treatment of data

Quality control was maintained by analyzing procedural and field blanks (during deployment, retrieval, and transportation to the laboratory) using the same procedures. All blanks were found to contain no analyte residues. All the validation studies were performed by using POCIS blank extracts taken through the entire processing and analysis procedure. For the studied pesticides, the mean recovery values (n=3) ranged between 79% and 114% while the relative standard deviation was less than 16% (Table 1). Calculated concentrations were not corrected by recoveries according to EU/SANCO guidelines (EU 2009). Precision of the method, determined as RSD, was obtained from the repeated analysis (n=3) of a spiked POCIS extract during the same day (repeatability) and in different days (reproducibility). The precision of the method was

Table 1 Selected physicochemical properties and mean percent recoveries (% RSD) of the target pesticides from lake water samples after SPE using Oasis HLB cartridges and from the pest-POCIS triphasic admixture

Pesticide	Class	CAS number	Solubility[a] (mg L^{-1}) (20°C)	Log K_{ow}[a]	Recovery SPE (n=3) (% RSD)	Recovery pest-POCIS (n=3) (% RSD)
Herbicides						
Alachlor	Chloroacetanilide	15972-60-8	240	3.09	95 (11)	96 (5)
Atrazine	*s*-Triazine	1912-24-9	35	2.70	86 (8)	79 (12)
Atrazine de-ethyl	Triazine metabolite	6190-65-4	3,200	1.53	103 (5)	87 (9)
s-Metolachlor	Chloroacetanilide	87392-12-9	480	3.05	91 (7)	81 (12)
Prometryne	*s*-Triazine	7287-19-6	33	3.34	95 (10)	87 (15)
Simazine	*s*-Triazine	122-34-9	5	2.30	93 (3)	98 (6)
Insecticides						
Chlorpyrifos	Organophosphate	5598-13-0	1.05	4.70	74 (7)	108 (10)
Chlorpyrifos methyl	Organophosphate	39475-55-3	2.74	4.00	94 (5)	112 (6)
Diazinon	Organophosphate	65863-03-8	60	3.69	97 (9)	92 (11)
Malathion	Organophosphate	121-75-5	148	2.75	94 (8)	114 (5)
Fungicides						
Benalaxyl	Anilide	71626-11-4	28.6	3.54	91 (9)	84 (9)
Pyrimethanil	Anilinopyrimidine	53112-28-0	121	2.84	105 (5)	97 (9)
Triadimenol	Triazole	55219-65-3	72	3.18	94 (7)	101 (12)

[a] Data from FOOTPRINT PPDB database (FOOTPRINT 2006)

considered satisfactory with RSD ranging from 1% to 5%. The instrumental and method detection limits (LODs) and quantification limits (LOQs) for the target pesticides were determined experimentally by measuring the coincident instrumental response of standard pesticide solutions and spiked blank POCIS extracts, respectively, using a signal to noise ratio (S/N) of 3 and 10, respectively. Method LODs and LOQs were estimated by substituting the determined limits in the sampler extracts into Eq. 3. (Zhang et al. 2008). LODs and LOQs ranged between 13 to 140 pg L^{-1} and 42 to 480 pg L^{-1}, respectively (Table 2). The mean recoveries (n=3) of the target pesticides by SPE ranged between 74% and 105% with RSD <14% (Table 1).

The regression lines for concentration factors of selected pesticides onto POCIS over the deployment time were fitted by linear regression models. The Origin Software for Windows (version Pro8, Microcal Software) was used for regression analysis. Quality of fit was characterized by relative standard deviations as well as by the correlation coefficient adjusted for the degrees of freedom (R^2 adjusted) and the Fisher test criterion for the accuracy of the model. The required variances of R_s values were calculated from the RSD of the uptake slope parameters (Vrana et al. 2006a; Tran et al. 2007). Significant differences in the R_s calculated in different time periods and by using different uptake models (fitted either through origin or the line of best fit) were tested by t-test

3 Results and discussion

3.1 Calibration and performance of POCIS

The uptake kinetic curves (based on the experimental concentration factors) of target pesticides in pest-POCIS after their exposure for 3, 7, 14, 21, and 28 days in filtered lake water are shown in Fig. 2. The uptake of pesticides in POCIS follows a linear pattern throughout the 28-day exposure. The correlation coefficients (Adj. R^2) of the linear regression ranged between 0.9214 and 0.9807 (Table 3) and the relative standard deviations of the calculated concentration factor, CF_t, remained between 3% and 26%, consistent with the findings of Mazzella et al. (2007). The relatively high RSD values could be due to the carbonaceous adsorbent contained in the POCIS triphasic sorbent admixture according to Mazzella et al. (2007). An analysis of variance of two uptake models (either fitted through origin or the line of best fit) showed no significant difference between the two models (p<0.001). The two models were significantly different only for chlorpyriphos and chlorpyriphos methyl for p<0.01. To simplify the calculation of R_s, the regression lines for each pesticide were fitted through origin. Linear regression models with zero intercept were employed also in other studies (Gunold et al. 2008; Zhang et al. 2008; Tran et al. 2007). Linear uptake kinetics over a 21-day period was also observed for atrazine, simazine, and metolachlor using SDB-XC Empore disk (Tran et al. 2007) as the receiving phase. Mazzella et al.

Table 2 GC–MS parameters used for identification and quantification of each target compound and limits of detection and quantification using SPE and POCIS

Pesticides	t_R	Identification/quantitation ions (m/z)	Pest-POCIS		SPE	
			LOD (ng L^{-1})	LOQ (ng L^{-1})	LOD (ng L^{-1})	LOQ (ng L^{-1})
Herbicides						
Alachlor	12.03	269, 188, 160	0.027	0.091	0.17	0.56
Atrazine	10.31	215, 200, 173	0.028	0.094	0.29	0.96
Atrazine desethyl	9.51	187, 174, 172	0.14	0.48	0.49	1.6
s-Metolachlor	13.10	238, 240, 162	0.020	0.067	0.06	0.21
Prometryne	12.29	241, 226, 184	0.035	0.12	0.10	0.32
Simazine	10.25	201, 186, 173	0.082	0.27	0.29	0.96
Insecticides						
Chlorpyrifos	13.15	314, 199, 197	0.14	0.45	0.41	1.4
Chlorpyrifos methyl	11.86	288, 286, 125,	0.027	0.091	0.15	0.49
Diazinon	10.64	179, 152, 137	0.074	0.25	0.86	2.9
Malathion	12.91	173, 127, 125	0.13	0.42	1.40	4.7
Fungicides						
Benalaxyl	19.58	206, 148, 132	0.013	0.042	0.12	0.41
Pyrimethanil	10.86	198 , 199, 77	0.024	0.081	0.26	0.87
Triadimenol	14.95	128, 168, 112	0.048	0.16	0.58	1.9

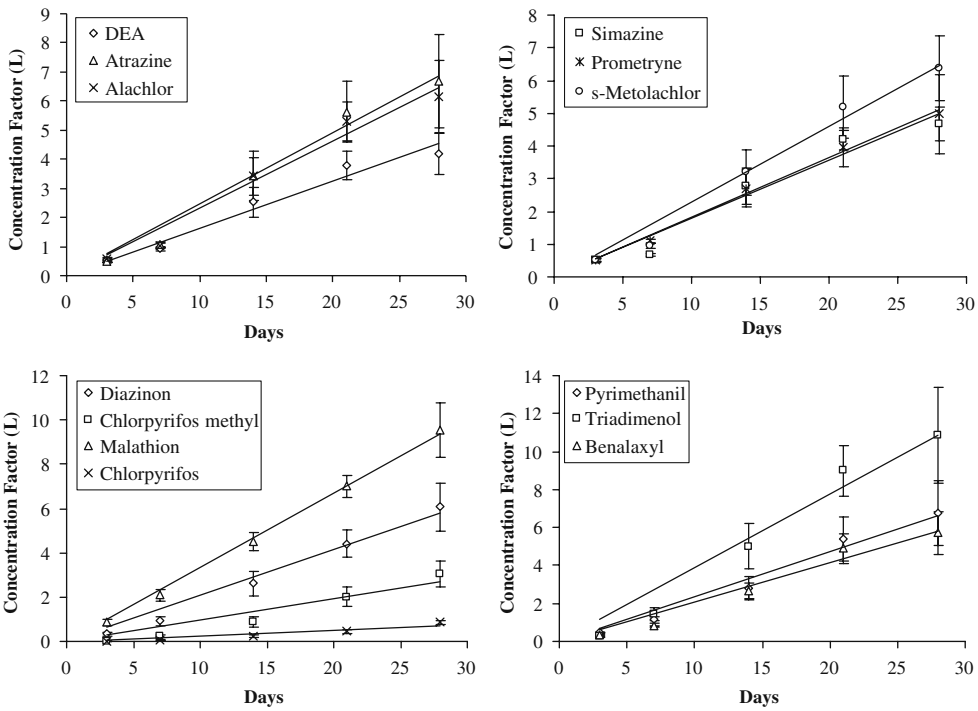

Fig. 2 Evolution of the experimental concentration factors (L) of the studied pesticides in pest-POCIS samplers over a 28-day exposure period under laboratory conditions

(2007) also reported linear uptakes for atrazine and simazine using POCIS-pharmaceutical configuration while a curvilinear uptake was observed for DEA.

Based on the calculated slope for each pesticide uptake, the mean sampling rates, R_s, varied from 0.025 for chlorpyrifos to 0.388 for triadimenol with RSD <29% (Table 3). The slight increase (burst effect) in sampling rates occurring in the first days as reported in Mazzella et al. (2007) with pharm-POCIS and Alvarez (1999) was not observed in this study. The increased sampling during the initial time of deployment is attributed to an increased flux of water crossing the membrane in an attempt to solvate or wet the polymer. On the contrary, a lag phase of about 3 days could be distinguished for the more hydrophobic pesticides with K_{ow}>4 such as chlorpyrifos and chlorpyrifos methyl. Due to the lag phase, the sampling rates for the two compounds were significantly different (p<0.01) when considering a deployment time of 14 days compared to longer deployment times (21 or 28 days). The lag time is attributed to the time it takes for the compound to initially pass through the diffusive barriers (water boundary layer, water in membrane pores and the membrane) (Shaw et al. 2009). Lag uptake for the more hydrophobic compounds may be due to sorption to the membrane surfaces dominating in the early stages, which may suggest biphasic uptake, or to mass transfer through the polymeric matrix (Harman et al. 2008; Kingston 2000). Vermeirssen et al. (2009) also observed that the lag phase over PES membrane in

Table 3 Calibration results for pest-POCIS sampler over 28 days in lake water under controlled laboratory conditions

Pesticides	R_s (L day^{-1})	RSD (%)	Linearity over 28 days (adj. R^2)
Alachlor	0.230	18	0.9697
Atrazine	0.245	21	0.9573
Atrazine desethyl	0.162	17	0.9715
s-Metolachlor	0.230	17	0.9716
Prometryne	0.182	18	0.9674
Simazine	0.178	16	0.9742
Chlorpyrifos	0.025	29	0.9214
Chlorpyrifos methyl	0.095	28	0.9252
Diazinon	0.207	17	0.9706
Malathion	0.308	14	0.9807
Benalaxyl	0.208	19	0.9646
Pyrimethanil	0.237	23	0.9511
Triadimenol	0.388	22	0.9549

Chemcatcher sampler with SDB-RPS as receiving phase increases with increasing hydrophobicity of the compounds studied (pesticides and pharmaceuticals). Diazinon, one of the most hydrophobic compounds studied, showed a lag phase of 2–3 days. The above effect, however, could not be significant for a typical 21 or 28 days' exposure (Harman et al. 2008; Alvarez et al. 2007); otherwise, for shorter deployment times (<7 days), the membrane should be co-extracted. Taking into account that for chlorpyrifos methyl and chlorpyrifos the lag time is significant while for DEA the calibration curves tend to in equilibrium, an optimal duration of 21 days could be proposed for POCIS exposure.

Some previous studies reported laboratory-derived R_s values for some of the target pesticides such as atrazine, simazine, DEA, malathion, and diazinon (Alvarez et al. 2000, 2007) using pest-POCIS (Table 4). Additionally, laboratory-derived R_s values of atrazine and simazine using pharma-POCIS were reported elsewhere (Mazzella et al. 2007; Martinez-Bueno et al. 2009). Such R_s values are comparable to the present study and differences can be explained taking into account the different experimental parameters (temperature, flow, etc.) affecting the sampling rates.

Figure 3 shows the relation between the log K_{ow} and the R_s of the pesticides. A nonlinear regression was performed for mean sampling rates, R_s, determined from the calibration experiments using a third-order polynomial function $(Y = P + aX + bX^2 + cX^3)$ of log K_{ow} $(y = 0.0028x^3 - 0.0936x^2 + 0.450x - 0.3338)$ $(p < 0.05$; $R^2 = 0.6323)$ as elsewhere (Vrana et al. 2006a; Mazzella et al. 2007; Shaw et al. 2009). An increase of the sampling rates with the hydrophobicity was observed for pesticides with log K_{ow} values up to 3 followed by a decrease thereafter especially for those with log K_{ow}>3.5. Shaw et al. (2009) reported a quite similar trend for the uptake with RPS-SDB sorbent phase across the compounds studied (log K_{ow} 1.78–4.0), while in other studies (Gunold et al. 2008; Arditsoglou and Voutsa 2008) no significant relationship between log K_{ow} and R_s was observed using SDB-XC and POCIS (pharm and pest configurations) for pesticides and selected endocrine disruptors, respectively. Recent work has provided some evidence of a Gaussian-shaped relationship between pharm-POCIS R_s and log K_{ow} for herbicides (Mazzella et al. 2007) with a plateau for log K_{ow} higher than 2.5. In addition, Vrana et al. (2006a) also observed a Gaussian-shaped relation between R_s for C18 sorbent and log K_{ow} for hydrophobic organic compounds such as PAHs and organochlorine pesticides using Chemcatcher passive sampler. Our results presented some evidence of a Gaussian-shaped relationship although that fewer compounds with K_{ow}<3 and more compounds with K_{ow}>3 are included in the present study compared to the previous one. It is unlikely

Table 4 Comparison of sampling rates of previously studied pesticides in various sorbents used in passive samplers

Receiving phase	Setup conditions				R_s values (L/day)					Reference
	Membrane	T, °C	Experimental setup	Stirring	Atrazine	DEA	Simazine	Malathion	Diazinon	
SDB-XC	PES	23	Flow through system	0.004 (m/s)	0.023		0.024			Tran et al. 2007
	–	14	Flow through system	0.14 (m/s)	0.22					Gunold et al. 2008
SDB-RPS	PES	22		0.14 (m/s)	0.17–0.19		0.17–0.19			Scott-Stephens et al. 2009
	PES	18.8	Flow through system		0.12	0.10			0.06	Vermeirssen et al. 2009
	PES	21.4	Batch chamber	0.14 (m/s)	0.14		0.14			Shaw et al. 2009
Pharm-POCIS		17±1	Microcosms	2–3 cm/s	0.239	0.1215	0.210			Mazzella et al. 2007
Pest-POCIS					0.240	0.260	0.220	0.005		Alvarez et al. 2007
									0.186	Alvarez et al. 2000
		22±1	Static renewals	480 rpm	0.245	0.162	0.178	0.308	0.207	This study
Pharm-POCIS		21	Static renewals		0.214		0.223			Martinez-Bueno et al. 2009

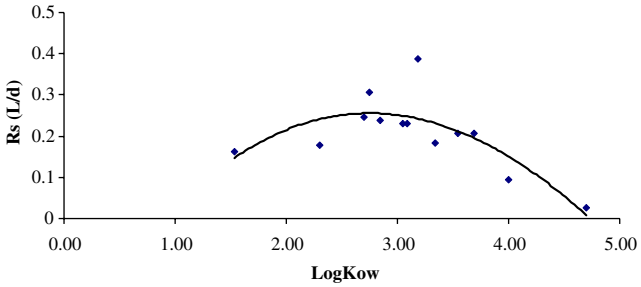

Fig. 3 Correlation between sampling rates, R_s (mL day^{-1}), and hydrophobicity, log K_{ow}, for the target pesticides

that K_{ow} itself is a satisfactory suitable descriptor to be able to predict sampling rates for compounds with diverse functional groups (Harman et al. 2008) as confirmed by the poor correlation coefficient (R^2) found. For example, atrazine, alachlor, and triadimenol (log K_{ow} 2.70, 3.09, and 3.18, respectively) had sampling rates of 0.248, 0.231, and 0.389 L day^{-1}, respectively. Additionally, chlorpyriphos methyl and chlorpyrifos (log K_{ow} 4.0 and 4.70) have sampling rates of 0.056 and 0.025 L day^{-1}, respectively. It is largely assumed that the R_s of polar analytes is highly controlled by the water boundary level (Alvarez et al. 2004; Macleod et al. 2007; Mazzella et al. 2008; Vermeirssen et al.

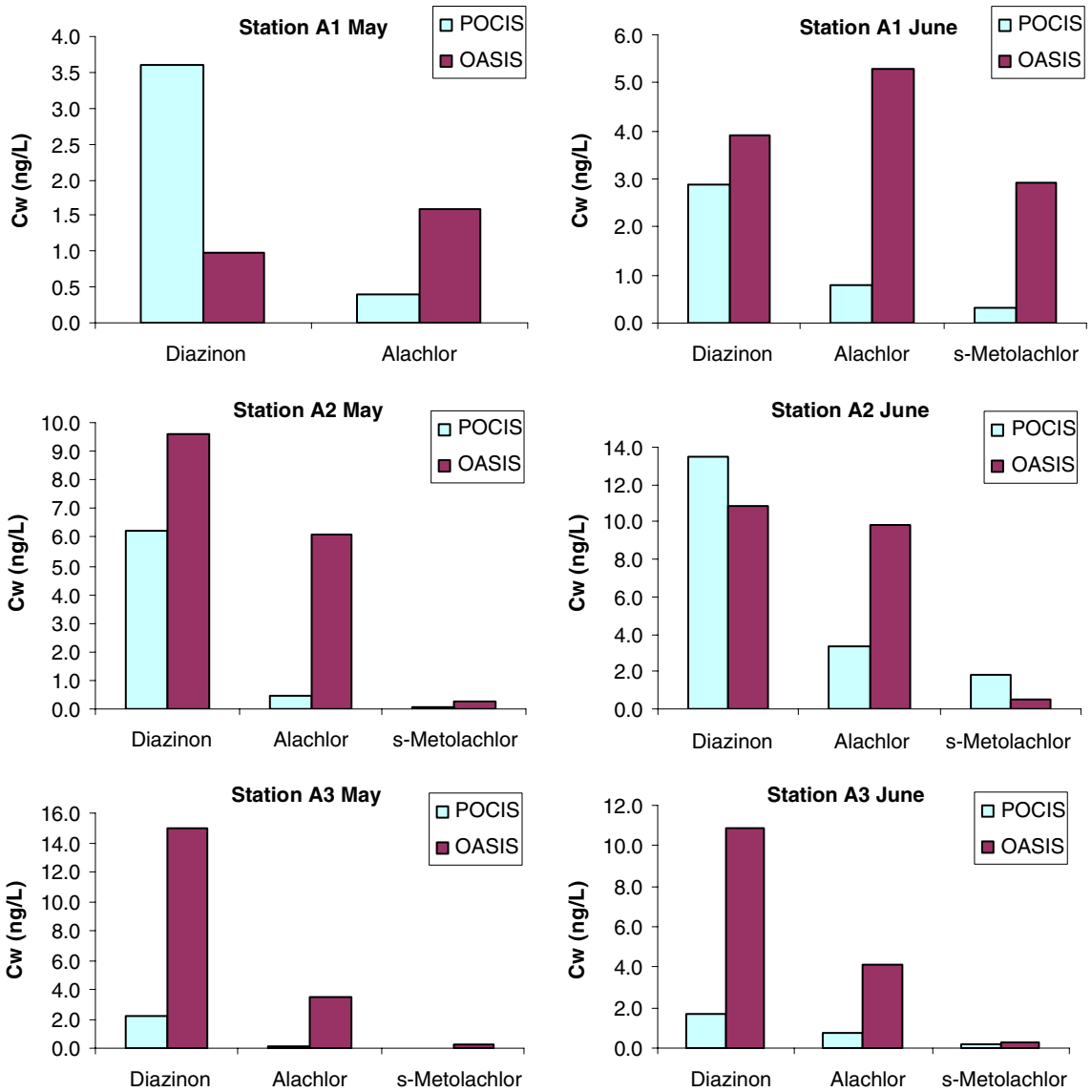

Fig. 4 Comparison of the pesticide concentrations determined by POCIS passive samplers deployed for 28 days and spot water sampling at the sampling sites in the Lake Amvrakia during May and June 2009

2009) and then by diffusion constants in water. Consequently, the polarity is not the only parameter to consider.

3.2 Field application

The analytical procedure was applied for the detection of the target contaminants in the Lake Amvrakia, Western Greece. The concentrations of pesticides in water after passive sampling were estimated from the amount of the individual pesticide in the exposed POCIS and the corresponding sampling rate value according to Eq. 3. The concentrations of the studied pesticides determined with POCIS and spot samples collected at the same sites are shown in Fig. 4. At the three sites, three of the 13 target pesticides were found with the POCIS passive sampler. Detection of pesticides is consistent with the major agricultural activities around the lake. Alachlor and *s*-metolachlor are mainly applied to corn cultivations while diazinon was applied in horticulture and olive tree cultivations. The pesticides alachlor and diazinon were detected more frequently and had the higher TWA concentrations reaching up to 3.32 and 13.5 ng/L, respectively. In general, pesticides exhibited lower concentrations using passive sampling than the concentrations determined using grab sampling. Only in three cases, for diazinon (A2, June 2009) and *s*-metolachlor (A2, A3, June 2009), were the concentrations from POCIS higher than those by spot sampling. Alvarez et al. (2004) showed also that the water concentrations from POCIS for diuron were much higher than those from spot sampling, while for isoproturon an opposite trend was observed.

Field conditions (water flow and turbulence, water temperature, biofouling, suspended solids, etc.) different from the conditions during calibration experiments in the laboratory could affect the sampling rates and the estimated water concentrations (Vrana et al. 2005; Togola and Budzinski 2007).

The presence of organic carbon can affect the dissolved fraction of waterborne contaminants. TWA concentrations estimated using POCIS samplers reflect a truly dissolved fraction of pesticides and those bound to particles with a cross-sectional diameter lower than 0.1 μm, the pore size of the membrane (Söderström et al. 2009). On the contrary, spot samples were filtered through 0.45-μm-pore-size filters and thus contained a higher contaminant fraction that is bound to dissolved organic material (DOM) present in water. The dissolved fraction of pesticides in water will depend on the level and quality of DOM which may fluctuate during the sampling period (Burkhard 2000; Greenwood et al. 2007). However, the adsorption of polar pesticides to DOM is generally low. Thus, the influence of DOM would be greater for the more hydrophobic compounds such as diazinon. Vrana et al. (2006a, b) also attributed the differences between water concentrations of PAHs obtained by active and passive sampling techniques to the presence of DOM. Another reason for the differences observed between spot and passive sampling may be the great variation during the sampling period, i.e., peak concentrations after short-term run-off events which will give higher concentrations when employing active sampling. On the contrary, the concentration peaks are smoothed out by time integration with passive sampling (Arditsoglou and Voutsa 2008).

Finally, the differences in the concentration levels derived from the two approaches could be due to the low frequency of the grab sampling (4 weeks between samples) especially for small drainage basins (<1,000 km^2) as in the present study area. Mazzella et al. (2008) studied the comparison of POCIS and SPE approaches for estimating herbicide concentrations during a microcosm experiment and concluded that the largest differences between the concentration levels derived from spot and passive sampling should be observed where the time resolution for grab samples is low.

In order to obtain accurate quantitative data of the contaminant concentrations, accurate field sampling rates remain a challenge for kinetic passive samplers by the use of performance reference compounds (PRCs), which represent analytically non-interfering chemicals (e.g., deuterium or ^{13}C-labeled compounds and native compounds not found in the environmental system of interest) that are added to a passive sampler prior to use (Huckins et al. 2002; Alvarez et al. 2007). Recently, the use of PRCs (DIA-*d5*) has been successfully applied for the assessment of the R_s in situ and correction of laboratory-derived sampling rates of POCIS for polar pesticides (Mazzella et al. 2010). The use of passive samplers could be successfully applied for (a) water quality monitoring including the pesticide screening and spatio-temporal distribution in various aquatic environments, (b) identification of specific contamination sources, (c) the assessment of the relative risk for various aquatic organisms, and (d) for conducting integrated monitoring studies by combining pesticide analysis with toxicity evaluation using various bioassays and toxicity tests (Söderström et al. 2009).

4 Conclusions

Laboratory experiments based on static renewals under stirred conditions were performed for the calibration of POCIS (pesticide configuration) and the calculation of sampling rates of the selected pesticides. The calibration revealed integrative uptakes of the target pesticides for 28 days. A lag phase for the more hydrophobic compounds and a poor correlation between hydrophobicity and sampling rates were observed. Using the described analytical proce-

dure, trace levels of the target pesticides could be determined (ng L^{-1}). A short monitoring campaign was conducted in Lake Amvrakia by passive and spot sampling for 2 months. Among the target pesticides, alachlor, *s*-metolachlor, and diazinon were detected. POCIS have been demonstrated suitable for the screening of a broad range of pesticides and they can give reasonable estimates of ambient concentrations, providing a holistic approach for the determination of pesticides in aquatic environments. More pronounced differences between pesticide concentrations obtained by spot sampling and passive sampling indicate that further work is needed in order to improve the performance of the passive samplers in different environmental conditions, addressing the feasibility of using PRCs on POCIS.

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