Environ. Sci. Technol. **2010,** *44,* 1713–1719

Evaluation of the Use of Performance Reference Compounds in an Oasis-HLB Adsorbent Based Passive Sampler for Improving Water Concentration Estimates of Polar Herbicides in Freshwater

NICOLAS MAZZELLA,*,† SOPHIE LISSALDE,*,† SYLVIA MOREIRA,† FRANÇOIS DELMAS,† PATRICK MAZELLIER,‡ AND JAMES N. HUCKINS§

Cemagref, UR REBX, 50 Avenue de Verdun, Gazinet, F-33612 Cestas Cedex, France, LPTC-ISM, UMR CNRS 5255, Université de Bordeaux - IUT de Périgueux. Rue du doyen Joseph Lajugie, 24019 Périgueux Cedex, and U.S. Geological Survey, Columbia Environmental Research Center, Columbia, Missouri 65201

Received July 27, 2009. Revised manuscript received December 16, 2009. Accepted December 21, 2009.

Passive samplers such as the Polar Organic Chemical Integrative Sampler (POCIS) are useful tools for monitoring trace levels of polar organic chemicals in aquatic environments. The use of performance reference compounds (PRC) spiked into the POCIS adsorbent for in situ calibration may improve the semiquantitative nature of water concentration estimates based on this type of sampler. In this work, deuterium labeled atrazine-desisopropyl (DIA-*d*5) was chosen as PRC because of its relatively high fugacity from Oasis HLB (the POCIS adsorbent used) and our earlier evidence of its isotropic exchange. In situ calibration of POCIS spiked with DIA-*d*5 was performed, and the resulting time-weighted average concentration estimates were compared with similar values from an automatic sampler equipped with Oasis HLB cartridges. Before PRC correction, water concentration estimates based on POCIS data sampling rates from a laboratory calibration exposure were systematically lower than the reference concentrations obtained with the automatic sampler. Use of the DIA-*d*5 PRC data to correct POCIS sampling rates narrowed differences between corresponding values derived from the two methods. Application of PRCs for in situ calibration seems promising for improving POCIS-derived concentration estimates of polar pesticides. However, careful attention must be paid to the minimization of matrix effects when the quantification is performed by HPLC-ESI-MS/MS.

Introduction

Over the past 20 years passive sampling devices have been developed that accumulate inorganic or organic micropollutants. Semipermeable membrane devices (SPMDs) (*1*) and more recently the Polar Organic Chemical Integrative Sampler (POCIS) (*2*) were used for the passive sampling of lipophilic and hydrophilic chemicals, respectively. These devices allow the passive concentration of organic chemicals from large volumes of water, resulting in ultratrace level detection, and smoothed integrative sampling. These techniques provide time-weighted average (TWA) concentrations that may be used for the application of regulatory programs (i.e., European Water Framework Directive 2000/60/EC (*3*)). However, it is well-known that rates of analyte accumulation in such devices are often affected by environmental exposure conditions like flow velocity, biofouling, and temperature (*4*−*9*). One of the most promising methods for overcoming this limitation consists of the use of PRCs (*10*). These compounds are spiked into samplers before deployment and if we assume isotropic exchanges, then both PRC dissipation and analyte uptake are theoretically equally affected by exposure conditions.

This work focuses on the potential use of a PRC for reducing errors associated with POCIS-derived water concentration estimates. In particular, the use of PRCs may reduce inaccuracy in environmental concentration estimates caused by the site specific effects of environmental conditions on POCIS sampling rates. For this purpose, desorption rate kinetics of some selected polar herbicides were monitored during a laboratory experiment. Afterward, in situ calibrations were performed and the use of DIA-*d*5 as PRC was investigated. As far as we are aware, no application of the PRC approach was previously developed for the POCIS. Potential matrix effects were also evaluated based on HPLC-ESI-MS/MS interferences present in POCIS extracts.

Experimental Section

Chemicals. Acetonitrile supragradient, methanol gradient, and water gradient (HPLC grade) were purchased from ICS-Science Groupe (Gradignan, France). GF/F glass fiber filters (47 mm diameter) were provided by Whatman (Versailles, France). Ultrapure water with a resistivity of 18 MΩ was used (Millipore, Guyancourt, France). Empty 1 mL polypropylene solid-phase extraction (SPE) tubes with polyethylene (PE) frits (20 μm porosity) and Oasis HLB bulk sorbent (60 μm) were purchased from Supelco (Saint-Quentin-Fallavier, France) and Waters (Guyancourt, France), respectively. Hydrophilic polyethersulfone (PES) SUPOR 100 Membrane Disc Filters (0.1 μm, 90 mm membrane diameter) were purchased from Pall (Saint-Germain-en-Laye, France). Oasis HLB cartridges (6 mL, 500 mg, 60 μm) were provided by Waters (France). Pharmaceutical POCIS were provided by Exposmeter (Tavelsjö, Sweden). All analytical standards were purchased from Dr. Ehrenstorfer (Germany): ametryn, atrazine, cyanazine, atrazine-desethyl (DEA), terbuthylazine-desethyl (DET), atrazine-desisopropyl (DIA), irgarol 1051, prometryn, propazine, simazine, terbuthylazine, terbutryn, chlortoluron, diuron, 1-(3,4-dichlorophenyl)-3-methylurea (DCPMU), 1-(3,4-dichlorophenyl)-urea (DCPU), fenuron, isoproturon, 1-(4-isopropylphenyl)-3-methylurea (IPPMU), 1-(4-isopropylphenyl)-urea (IPPU), linuron, metobromuron, metoxuron, monolinuron, Monuron, neburon, acetochlor, alachlor, metolachlor, metazachlor, DIA-*d*5, DEA-*d*6, atrazine-*d*5, diuron-*d*6, metolachlor-*d*6.

Automatic Water Samplers. 6712 Full-size portable samplers (Teledyne ISCO, U.S.) were used for determining the reference time-weighted average (TWA) concentrations. The automatic water samplers were operated with a uniform time sampling mode. The sampling frequency and volume were hourly and 50 ± 5 mL, respectively. The TWA con-

* Address correspondence to either author. Phone: + 335 57 89 27 18. Fax: +335 57 89 08 01. E-mail: nicolas.mazzella@cemagref.fr (N.M.); sophie.lissalde@cemagref.fr (S. L.).
† Cemagref.
‡ Université de Bordeaux.
§ U.S. Geological Survey.

10.1021/es902256m
Published on Web 01/28/2010

centrations were obtained with the collection of the hourly samples into a 19 L glass bottle. The glass bottles were kept in the dark and collected every week during the exposure period.

Suspended Particulate Matter and Organic Carbon Determinations. Water samples (1 L) were filtered through Whatman GF/F glass microfibre filters (0.7 μm pore size) for the determination of suspended particulate matter (SPM), and total and dissolved organic carbon (TOC and DOC) content. SPM were weighted according to the standard NF EN 872 (*11*). Both TOC and DOC content were measured using a model 1010 OI analytical carbon analyzer with a 1051 autosampler (Bioritech, France).

Solid Phase Extraction. Preconcentration of the analytes from water samples was accomplished by using solid-phase extraction (SPE) with Oasis HLB cartridges. Prior to SPE, 200 mL water samples (pH adjusted to 7) were filtered using GF/F glass microfibre filters. Then, an isotopic dilution (*12*) was performed with the addition of 10 μL of a stock solution (acetonitrile) containing 10 ng μL^{-1} of DEA-*d*6, atrazine-*d*5, diuron-*d*6, and metolachlor-*d*6 was added, resulting in fortification of the water samples with 0.5 $\mu g\ L^{-1}$ of each internal standard. SPE was conducted using a VisiPrep 12-port manifold from Supelco (Saint-Quentin-Fallavier, France). The conditioning, extraction, and rinsing steps were carried out under a 53.33 kPa vacuum. The SPE cartridges were successively washed with 10 mL of methanol, conditioned with 10 mL of HPLC grade water, loaded with 200 mL of water samples, rinsed again with 20 mL of HPLC grade water, and dried with a stream of nitrogen for 30 min. Analytes were eluted with 5 mL of methanol. The 5 mL extracts were blown under a gentle stream of nitrogen and dissolved in 1 mL of an acetonitrile:water (10:90, v/v) mixture prior to the HPLC-ESI-MS/MS analyses.

POCIS Sorbent Spiking. "Pharmaceutical" POCIS (*2*) contains 200 mg of Oasis HLB sorbent enclosed between two polyethersulfone (PES) membranes. The membrane-sorbent-membrane layers are compressed between two holder washers (5.1 cm i.d., 8.9 cm o.d.). The total exchanging surface area of the membrane (both sides) is approximately 41 cm^2 and the surface area per mass of sorbent ratio is approximately 200 $cm^2\ g^{-1}$.

For the microcosm desorption experiment, 10 μg of atrazine, DEA, DIA-*d*5, simazine, isoproturon, and metolachlor were dissolved in 25 mL of methanol. This solution was added to 5 g of Oasis HLB bulk sorbent and sonicated for 5 min. The solvent was removed with a rotary evaporator, and the sorbent was dried at 60 °C for 1 h. This procedure provided 5 g of Oasis HLB bulk sorbent spiked with about 2 $\mu g\ g^{-1}$. Three reference cartridges were prepared by transferring 200 mg of the fortified sorbent into 1 mL empty polypropylene SPE tubes with PE frits. These references are used for determining both the initial spike concentration and homogeneity. Eleven POCIS were prepared with 200 mg of the same fortified sorbent enclosed between two PES membranes (0.1 μm pore size). These POCIS were exposed in microcosms under quiescent or turbulent conditions. For the field experiments, the same protocol was used and the sorbent was spiked with DIA-*d*5 only (2 $\mu g\ g^{-1}$).

Microcosm Experimental Design. A large volume microcosm (up to 80 L) filled with tap water (pH 7.3) was used for the desorption experiment. The microcosm setup and experimental conditions (i.e., temperature, flow velocity, darkness, and $CuSO_4$ addition) were described in a previous work (*13*). A background blank control microcosms was carried out simultaneously. Eight spiked POCIS were immersed into the microcosm and duplicates were collected after 7, 14, 21, and 28 days. Residues accumulated in POCIS were analyzed by HPLC-ESI-MS/MS for determining desorption kinetic rate constants. Three other spiked POCIS were exposed during 28 days with the same experimental conditions except the flow velocity (quiescent conditions). This POCIS was used as control for the desorption rates and the eventual degradation of the analytes within the receiving phase.

Field Deployment of POCIS. All POCIS were exposed in high density polyethylene deployment devices. The POCIS orientation was vertical with the PES membranes perpendicular to the water surface (*14*) and the flow. The cages were immersed in a stream (Le Ruiné, a stream in the west part of France) and a large river (La Charente, west part of France). Both sites were equipped with an automatic water sampler giving weekly average concentrations.

For the in situ calibration exposure, six POCIS were exposed in the stream waters and duplicates were collected after 6, 13, and 22 days (from April 10th to May 2nd, 2007). For the PRC application and the comparison between POCIS and automatic water sampler TWA concentrations, triplicates of POCIS spiked with DIA-*d*5 were immersed and changed every 14 days (from April 28th to July 7th) in both stream and river waters.

POCIS Recovery. After the exposure in tap water (microcosm desorption study), each POCIS was opened and the receiving phase (i.e., Oasis HLB) was recovered in a 50 mL glass beaker with 2 × 20 mL washes of HPLC grade water. The sorbent was transferred into a 1 mL empty SPE tube with a PE frit and packed under vacuum by using a Visiprep SPE Manifold. Afterward, another polyethylene frit was added to the top of the SPE cartridge. All the cartridges were washed with 20 mL of HPLC grade water and dried with a stream of nitrogen for 30 min. Analytes were eluted with 5 mL of methanol. As for SPE, an isotopic dilution (*12*) was performed prior to the analysis: 10 μL of a stock solution (acetonitrile) containing 10 ng μL^{-1} of DEA-*d*6, atrazine-*d*5, diuron-*d*6, and metolachlor-*d*6 was added before the evaporation of the methanol with a gentle stream of nitrogen. The extracts were dissolved in 1 mL of an acetonitrile:water (10:90, v/v) mixture prior to the HPLC-ESI-MS/MS analyses. Matrix effects were evaluated and corrected with one-point standard additions (100 $\mu g\ L^{-1}$) in the POCIS extracts.

External surfaces of PES membranes from field exposed POCIS were carefully cleaned with ultrapure water for removing particles and organic matter. The sorbent was recovered as described above.

HPLC Separation and ESI-MS/MS Detection. The HPLC system consisted of a Finnigan SpectraSYSTEM SCM1000 Solvent Degasser, Finnigan SpectraSYSTEM P4000 Quaternary Pump, Finnigan SpectraSYSTEM AS3000 Autosampler (column oven set at 40 °C) and a Finnigan UV6000LP photodiode array detector (Thermo Electron Corporation, MA). Samples were pumped through a C_{18} (10 × 4 mm, 6 μm) guard column (Bischoff Chromatography, Germany) prior to separation with a Prontosil Spheribond ODS 2 column (150 × 4 mm, 3 μm). The injection volume and solvent composition were 50 μL and acetonitrile:water (10:90, v/v), respectively. Further details regarding to the binary gradient composition are given elsewhere (*12*).

The HPLC system was coupled with an API 2000 (Applied Biosystems/MDS SCIEX, France) triple quadrupole mass spectrometer equipped with a turboionspray source (ESI). Multiple reaction monitoring (MRM) mode and internal standards were used for the analyte quantifications. Further details related to the MRM transitions (except DIA-*d*5 with the 179 > 101 transition), internal standardization, and source parameters are given in a previous work. Matrix effects were evaluated and corrected, if necessary, with standard additions into POCIS extracts.

Theory and Modeling. Oasis HLB is classified by its manufacturer as a hyper-cross-linked porous polymeric adsorbent and not a partitioning medium. Thus, chemical

uptake and release (desorption) by Oasis HLB is generally not expected to follow overall first-order kinetics (*14, 15*) or to exhibit pure isotropic exchange. However, under certain conditions an adsorbent such as Oasis HLB may mimic first-order isotropic chemical exchange similar to the partitioning mediated semipermeable membrane devices (*1*). For example, an adsorbent may exhibit pseudofirst order linear exchange kinetics when exposure locations have trace levels of analytes and competing organic solutes, the adsorbent chosen is homogeneous in nature, and adsorption sites are of approximately equivalent energy for a particular solute. If we assume that analyte adsorption on Oasis HLB is reversible and monophasic, then it is reasonable to assume that adsorption kinetics will exhibit a first-order dependence on the concentration of vacant sites and that desorption kinetics will exhibit a first-order dependence on the concentration of the adsorbed analyte. These assumptions are representative of simple kinetic derivation of the Langmuir isotherm. In this case, we can apply as an approximation the following two compartment model:

$$C_{\mathrm{POCIS}} = \bar{C}_{\mathrm{w}} K_{\mathrm{sw}} (1 - e^{-k_{\mathrm{e}} t}) \quad (1)$$

where C_{POCIS} is the concentration (μg g^{-1}) of the analyte in the adsorbent, $\bar{C}_{\mathrm{w}}$ is the TWA concentration (μg L^{-1}) of the same analyte in water, and the K_{sw} (L g^{-1}) can be viewed as the equilibrium adsorption coefficient, which corresponds to the sampler-water partition constant (K_{p} or K_{sw} for SPMDs) in partitioning media.

For a two compartment model, the elimination rate constant k_{e} (d^{-1}) is defined as follows (*4*):

$$k_{\mathrm{e}} = \frac{R_{\mathrm{s}}}{K_{\mathrm{sw}} M_{\mathrm{POCIS}}} \quad (2)$$

where M_{POCIS} (g) is the mass of the sorbent within the POCIS and R_{s} (L d^{-1}) the sampling rate.

Both kinetic and equilibrium regimes (*16*) have been observed for the accumulation of polar pesticides by POCIS in previous work (*13*). However, POCIS generally acts as an infinite sink (i.e., zero-order uptake) for analytes with $1.5 \leq \log K_{\mathrm{ows}} \leq 4.0$ and this linear uptake generally lasts for several weeks (*2*). In this case, TWA concentrations of each analyte can be estimated by

$$\bar{C}_{\mathrm{w}} = \frac{m}{R_{\mathrm{s}} t} \quad (3)$$

where m (μg) is the amount of the analyte accumulated in the receiving phase of a passive sampler after an exposure time t (days). All adsorbent based passive samplers exhibit a linear uptake phase where analyte concentrations are proportional to exposure level. Pawliszyn suggested the use of a similar model for porous polymeric coated adsorbent fibres used in solid phase microextraction which is as follows (*17*):

$$\bar{C}_{\mathrm{w}} = \frac{m\delta}{B D_{\mathrm{s}} S t} \quad (4)$$

Where δ is the boundary layer thickness, D_{s} is the diffusion coefficient of the analyte in the surrounding water, S is the surface area of the sampler, and B is a geometric factor related to the configuration of the receiving phase such as a disk, cylinder, etc. By analogy, the sampling rates can be written as follows:

$$R_{\mathrm{s}} = k_0 S = \frac{B D_{\mathrm{s}}}{\delta} S \quad (5)$$

With k_0 the overall mass transfer coefficient which depends on δ if we assume that the analyte uptakes are mainly under boundary layer control (*2, 18*).

The use of an adsorbent with relatively low surface area (i.e., < 300 m^2/g) and specificity (i.e., low capacity for analytes of interest) may result in a rapid deviation from linear uptake. Oasis HLB has a relatively high surface area (i.e., of ~800 m^2 g^{-1}) and excellent specificity/capacity for many polar pesticides as well as many pharmaceuticals. Thus, assuming isotropic exchange of analytes and similar compounds, PRC can be used to correct for sampling rate fluctuations of passive samplers related to environmental conditions (*10*). A PRC is a compound that has moderate to high fugacity from the passive sampler sorbent, which does not interfere with the sampling and analytical processes and which is added to the device receiving phase prior to deployment. Under conditions of isotropic exchange, the elimination rate constant k_{e} of a PRC from the passive sampler sorbent can be determined with the following first-order relationship

$$k_{\mathrm{ePRC}} = \frac{\ln(C_{\mathrm{PRC0}} / C_{\mathrm{PRC}(t)})}{t} \quad (6)$$

where $C_{\mathrm{PRC}(t)}$ is the residual concentration (μg g^{-1}) of PRC in the receiving phase after an exposure time (t) and C_{PRC0} is the concentration of PRC spiked into the receiving phase before the exposure. When the elimination rate constant of a same PRC is determined under both calibration (k_{ePRCcal}) and the field ($k_{\mathrm{ePRCinsitu}}$) conditions, then the real value of the field sampling rate (R_{sinsitu}) can be approximated with a corrected value of the calibrated sampling rate (R_{scal}) as follows:

$$R_{\mathrm{scorr}} = R_{\mathrm{scal}} \times \left(\frac{k_{\mathrm{ePRCinsitu}}}{k_{\mathrm{ePRCcal}}} \right) \quad (7)$$

Several PRCs are generally necessary for the correction of the effects of environmental variables such as temperature, biofouling, and turbulence on a wide range of chemicals (*10, 19, 20*). For a correction of the sampling rate with only one PRC, we assume that the kinetics of the selected PRC and the kinetics of the pollutant uptake are closely related. As mentioned above, POCIS chemical exchanges are generally under boundary layer control (*2, 7*). In that case, this assumption is reasonable because rates of diffusion across aqueous boundary layers are largely affected by boundary layer viscosity and solute molecular weight or volume (*18*).

Results and Discussion

Laboratory Determination of the Kinetic Elimination Rate Constants. The elution and the HPLC-ESI-MS/MS analysis of the reference cartridges revealed initial concentrations (C_0) of 1.88 ± 0.04 μg g^{-1} (atrazine), 1.57 ± 0.04 μg g^{-1} (DEA), 1.73 ± 0.14 μg g^{-1} (DIA-*d*5), 1.75 ± 0.02 μg g^{-1} (simazine), 1.69 ± 0.06 μg g^{-1} (isoproturon), and 1.55 ± 0.02 μg g^{-1} (metolachlor). These results showed that spikes of the POCIS sorbent before the exposure were uniformly applied.

After 28 days of exposure in microcosms under quiescent conditions, analysis of the three spiked POCIS revealed relatively small losses of the analytes, even for DIA-*d*5. Desorption losses were lower than 10% (and close to the instrumental uncertainty and precision limits) for atrazine, DEA, isoproturon, metolachlor, and simazine and about 35% for DIA-*d*5. These results indicated that degradation of test chemicals adsorbed on Oasis HLB during these exposures was low. Concerning the POCIS exposed under turbulent conditions, desorptive losses were higher and ranged between 35 and 40% for atrazine, DEA, simazine, isoproturon, and metolachlor, while DIA-*d*5 desorption was about 90% (Figure 1). These results are in good accordance with a previous desorption kinetic study and confirm the relatively high

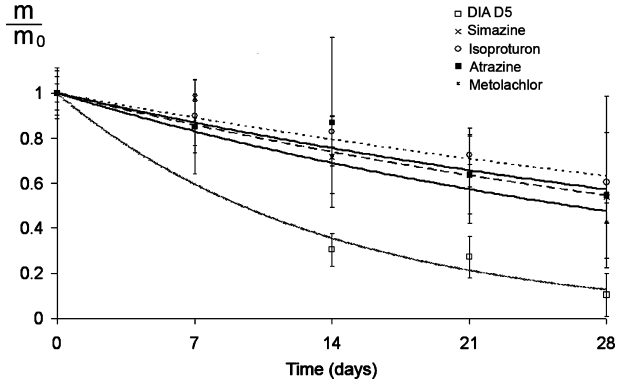

FIGURE 1. Desorption kinetic curves of DIA-*d*5, simazine, isoproturon, atrazine, and metolachlor from POCIS during 28 days of turbulent exposure.

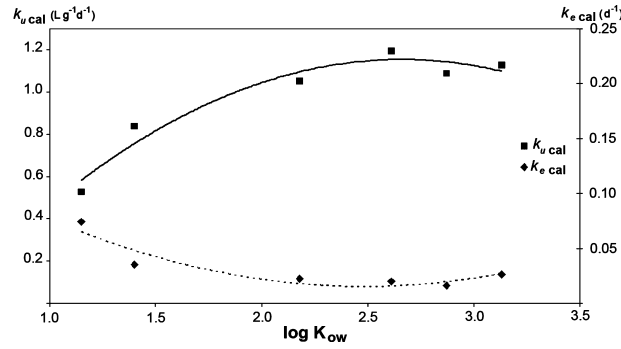

FIGURE 2. Evolution of k_{ucal} (*13*) and k_{ecal} (Table 1) of DIA-*d*5, DEA, simazine, isoproturon, atrazine, and metolachlor as a function of log K_{ow}.

fugacity of DIA (*13*). These findings are also in agreement with the previous works related to the calibration of polar chemicals (*2, 8*), and indicated that the kinetic exchange of all the chemicals of interest are likely under aqueous boundary layer control. In this case, if we consider eq 7, then we have to provide a correction for the variation of the boundary layer thickness (i.e., flow velocity) during field deployments.

The elimination rate constant k_{ecal} was calculated for each test chemicals and reported in Table 1. In a previous work (*13*), the k_e derived from the DIA uptake under the same turbulent conditions was about 0.08 ± 0.02 d^{-1}. This value compares favorably with the k_{ecal} determined in this work for the same compound (0.057 ± 0.006 d^{-1}). Although masses of DIA-*d*5 remaining in the samplers after 21 and 28 days of exposure do not appear significantly different and mean masses for 14 and 21 days appear similar (Figure 1), our earlier comparison between the k_{ecal} values has suggested isotropic exchanges of DIA-*d*5 and its potential application as PRC. We observed pseudofirst order kinetic desorption for all the analytes of interest (Figure 1) and the plot of both k_{ucal} and k_{ecal} as a function of the compound log K_{ow} (Figure 2) revealed symmetrical curves. The k_{ucal} values increased with the hydrophobicity whereas a decrease of the k_{ecal} values is observed. Globally, the log K_{sw} values, which reflect the affinity of each chemical with the receiving phase of the POCIS, increase with the hydrophobicity. However, the polar PES membrane is expected to limit the sampling rates of compounds with log $K_{ow} > 3.1$ as indicated by Figure 2. There was only one test compound with a log $K_{ow} > 3.1$ but diffusion through the polar polyethersulfone membrane is likely the rate limiting factor for compounds with log $K_{ows} > 3.0$. In fact, it was suggested that low sampling rates of hydrophobic organic compounds observed for nonpolar hexane enclosed by a polar cellulose membrane are due to the low permeability of hydrophobic solutes through a polar, water saturated membrane (*21*). In other words, uptake rates are controlled by the membrane in this case and not by the boundary layer, and resistance to mass transfer increases to some maximum as log K_{ows} increase.

Matrix Effects and HPLC-ESI-MS/MS Interference Evaluation. It is well-known that electrospray ionization suffers from matrix effects. Occurrence of polar/ionic compounds other than the analytes of interest, such as those originating from the sample matrix, may induce ion suppressions (*22, 23*). It may well affect both accuracy and precision. Different methods can be used for overcoming the matrix effects: the complete removal of coeluting substances by sample cleanup techniques such as gel permeation chromatography or solid phase extraction (*24*). Alternatively, the calibration standards can be made in a matrix extract rather than in a pure solvent (*25, 26*). Another common approach is based on the standard additions. Such a method provides both good accuracy and precision but the main disadvantage is that further analyses must be performed. Lastly, the use of internal standards would improve both accuracy and precision (*26, 27*), but appropriate internal standards are sometimes not available. The matrix effects were extensively studied in a previous work with various natural waters (*12*). An isotopic dilution technique was chosen for the minimization of the interferences with the use of deuterium labeled internal standards (DEA-*d*6, atrazine-*d*5, diuron-*d*6,and metolachlor-*d*6). This technique was successful with solid phase extracts of water samples, but not with the POCIS samples. In fact, one of the advantages of the passive sampling techniques is the high preconcentration of the hydrophilic pollutants. However, some polar interfering compounds may be preconcentrated simultaneously; resulting in severe matrix effects for the POCIS exposed in situ (Table 2). Polar herbicides and especially DIA-*d*5 may be highly affected, providing inaccurate or imprecise $k_{ePRCinsitu}$ estimates. Thus, correction with one-point standard addition was necessary. Multipoint standard additions are more accurate but this approach is really time-consuming and not applicable for routine moni-

TABLE 1. Values of log K_{sw} and k_{ecal} Determined during the Microcosm Experiment, and Values of $k_{einsitu}$ and $R_{sinsitu}$ Determined in April−May 2007 (in situ calibration of the POCIS in the Ruiné waters) and R_{scorr} Calculated with the PRC $k_{einsitu}$

hrbicides	log K_{ow}[a]	log K_{sw}	k_{ecal} (d^{-1})	$k_{einsitu}$ (d^{-1})	R_{scal} (L d^{-1})[d]	$R_{sinsitu}$ (L d^{-1})	R_{scorr} (L d^{-1})
DIA/DIA-*d*5 (PRC)	1.15	3.85	0.057 ± 0.006	0.022 ± 0.001	0.106 ± 0.017	0.025 ± 0.002	0.041 ± 0.016
DEA	1.40	4.38	0.024 ± 0.008	U.[b]	0.167 ± 0.027	0.061 ± 0.005	0.064 ± 0.026
simazine	2.18	4.68	0.022 ± 0.002	U.[b]	0.210 ± 0.001	0.063 ± 0.009	0.081 ± 0.022
DET	1.98	U.[b]	U.[b]	U.[b]	0.205 ± 0.006	0.075 ± 0.009	0.079 ± 0.022
atrazine	2.61	4.78	0.020 ± 0.013	U.[b]	0.239 ± 0.008	0.059 ± 0.008	0.091 ± 0.029
isoproturon	2.87	4.83	0.016 ± 0.010	U.[b]	0.218 ± 0.010	N.D.[f]	U.[b]
metolachlor	3.13	4.63[c]	0.027 ± 0.005	U.[b]	0.225 ± 0.016[e]	N.D.[f]	U.[b]

[a] log K_{ow} for pH 7−8 (*32*−*34*). [b] Unknown. [c] Metolachlor K_{sw} estimated with acetochlor k_{ucal} (*13*). [d] R_{scal} from Mazzella et al. (*13*). [e] Metolachlor R_{scal} estimated with acetochlor R_{scal} (*13*). [f] Not detected.

TABLE 2. Matrix Effects Observed for Some Selected Pollutants and Environmental Parameters (Suspended Particulate Matters, Dissolved and Total Organic Carbon, and Average Flow Velocities) Measured for the Two Sampling Sites (Le Ruiné and La Charente)

		% deviations[a]								
sampling	exposure periods	Atrizine	DIA	Diuron	Terbuthylazine	DIA-*d*5	SPM (mg L^{-1})	DOC (mg L^{-1})	TOC (mg L^{-1})	average flow velocities (cm s^{-1})[b]
	April 28th - May 13th	89	76	95	92	94	217.50	3.82	36.31	
	May 13th - May 26th	81	105	91	89	164	580.28	4.61	43.25	
	May 26th - June 9th	83	107	93	92	231	32.80	5.01	5.89	
	June 9th - June 23rd	89	111	86	100	175	394.70	4.30	12.20	
Ruiné	June 23rd - July 7th	96	103	89	97	175	445.25	3.79	12.14	<1
	April 28th - May 13th	79	88	83	76	107	17.80	3.57	28.60	
	May 13th - May 26th	82	110	111	123	113	4.90	3.32	18.10	
	May 26th - June 9th	82	124	108	123	134	17.10	3.77	4.34	
Charente	June 23rd - July 7th	91	111	112	113	138	12.70	3.13	4.43	1−2

[a] Relative deviations calculated with standard additions in POCIS extracts. Ratio between the measured and the expected concentrations. [b] Flow velocities were measured within the deployment devices.

toring. A compromise could be to look at differences in precision and accuracy by using a two standard addition approach.

In Situ Calibration of the POCIS. Replicate of POCIS were immersed in a stream (Le Ruiné, west part of France) during spring 2007 (from April 10th to May 2nd 2007). Only atrazine, DEA, DET, DIA, and simazine were detected both in water samples and POCIS during the whole exposure. For each compound, the concentration factor was calculated according to the ratio between the analyte amount within the POCIS and the TWA concentration of the same analyte in water samples during the corresponding exposure time. The POCIS were exposed perpendicular to the water flow during the field deployment. As stated by Alvarez et al. (*2*), the membrane itself can contribute a significant resistance to mass transfer. The analyte flux through the membrane occurs via a biphasic mechanism of transport in water-filled pores and diffusion in the polymeric matrix of the PES membrane. Due to the very small porosity (0.1 μm) and the tortuosity of the pores, we assume that the water in the membrane pores remains essentially stagnant and no water flow could pass directly through the sampler. Furthermore, some of the adsorbent accumulated at the bottom of the membrane envelope with the vertical orientation and therefore was not homogeneously distributed in the sampler. However, the vertical orientation of POCIS disk was also used for the calibration of the analytes (*13*) and the determination of the kinetic elimination rate constants. Consequently, there were no differences between both calibration and the deployment configurations and it is expected that the use of a PRC corrects for any change in configuration. The in situ analyte uptake curves are shown in Figure 3. Satisfactory linear regression fits of the eq 3 to the uptake data of analytes from water to POCIS were obtained for all the compounds of interest. The corresponding $R_{sinsitu}$ were calculated and reported in Table 1. The $R_{sinsitu}$ are about 3−4 times lower than the R_{scal}. This lower sampling rates observed in the field may be attributed to a lower temperature, a lower flow velocity or an eventual membrane biofouling (*5, 10, 20*). We did not observe any biofouling on the POCIS membranes and it has been reported that hydrophilic PES membranes are not really affected by biofilm formations (*2, 7, 16*). However, we did notice some depositions of SPM on the POCIS membrane surfaces. During the exposure, high SPM amounts were measured (about 1 g L^{-1}). An average temperature of 16 °C was measured during the during the field exposure. This value was close to the temperature chosen for the laboratory calibration (17 ± 1 °C) (*13*) and, consequently, the influence of this parameter on the sampling rate variations was probably negligible. Regarding the POCIS and some other polar passive samplers, several reports (*2, 7−9, 28*) indicate a preferential control of

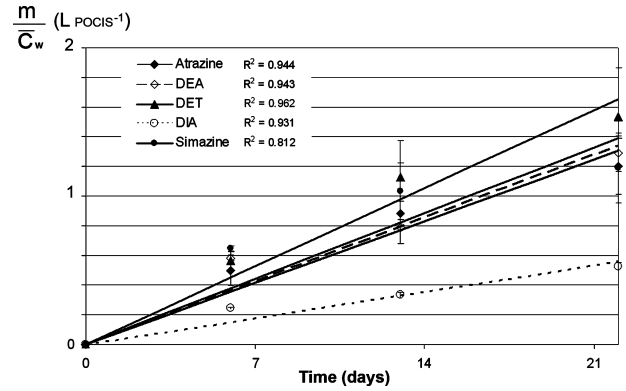

FIGURE 3. In situ variation of the concentration factors ($m/\bar{C}_w$) of atrazine, DEA, DET, DIA, and simazine after 6, 13, and 22 days of exposure in the streamwater (from April 10th to May 2nd 2007).

the solute mass transfer by the aqueous boundary layer. The flow velocity of the stream was relatively low (<1 cm s^{-1}), resulting in near quiescent conditions inside the deployment devices. Thus, the high differences between the $R_{sinsitu}$ and R_{scal} are probably due to the higher flow velocities used for the calibration (2−3 cm s^{-1}) (*13*).

If we apply the R_{scal} in this case, the concentrations are highly underestimated. Ideally, we must apply appropriate $R_{sinsitu}$ but field calibrations are time-consuming. In addition, calibrations must be representative of each sampling site and they should cover any environmental variations (e.g., temperature evolution with seasons or higher flow velocity during a flood) for a same sampling site. Alternatively, $R_{sinsitu}$ can be approximated with the use of appropriate performance reference compounds. The PRC approach was successfully developed and applied for the SPMDs (*10, 29*) and if we refer to the previous desorption kinetic study, we suggest the use of the DIA-*d*5 as PRC. Each POCIS used for the field calibration was spiked with a known amount of DIA-*d*5, the desorption kinetics was monitored, and the corresponding $k_{einsitu}$ was calculated (eq 6). The R_{scorr} were determined with the application of eq 7 (Table 1). The R_{scorr} values compare very favorably with the $R_{sinsitu}$ values since there is no significant differences between the sampling rate values (*t* test, $\alpha = 0.05$). Such a result show the potential use of the DIA-*d*5 as PRC for some triazines (atrazine and simazine) and their metabolites (DEA, DET, and DIA) and must be confirmed for other calibrated herbicides (*13*) like phenylureas and chloroacetanilides. The applicability of this PRC approach should be also studied with other in situ conditions such as higher flow velocities, different temperatures, and variable DOC

amounts. DOC includes nontargeted solutes, and competitive adsorption may occur between these interfering compounds and the analytes of interest. Competitive adsorption by nontargeted solutes depends on the relative magnitudes of the adsorption coefficients of the analytes and the competing solutes and the concentrations of the nontargeted solutes. Although DOC concentrations were measured (Table 2), this data provides no information of the individual concentrations of solutes comprising the DOC or their adsorption coefficients. Therefore, caution must be used in assuming that PRCs in POCIS at other sites with similar DOC levels will be free of competitive adsorption effects. Clearly, if these unknown solutes had significantly impacted PRC desorption rates, this would have adversely affect PRC-based concentration estimates, which was not the case in this study.

in Situ Application of the DIA-*d*5 as PRC. As for the in situ calibration, TWA reference concentrations were determined with automatic samplers. The stability of the test chemicals was studied for 10 days at room temperature in spiked water from the River Le Ruiné. No significant degradation was observed during this period (data not shown) for these compounds. Furthermore, the stability of these compounds are well-known in river waters and the half-life is longer than a week (i.e., 86 days for atrazine, 46 days for simazine, and even more persistent for diuron and acetochlor (*30*)). In regard to POCIS in tap water, we previously mentioned that there was no significant hydrolysis of the analytes sorbed in the devices over 28 days. Finally, the 0.1 μm pores of the membrane ensure that microorganisms can not access the POCIS adsorbent.

This passive sampling technique generally allows quantification of chemicals at ultratrace levels. Such levels are generally not accessible with the conventional SPE approaches. Very low TWA concentrations of simazine, diuron, DCPMU, and acetochlor (Figure 4a and b) were detected and quantified (ng L^{-1} level) with the POCIS. From April 28th to May 13th, the POCIS estimates were about twice as low than the reference TWA concentrations for the Charente river (Figure 4a) and about three times lower for the Ruiné stream (Figure 4b). As previously mentioned, these deviations from the reference values can be attributed to the relatively low average flow velocities, especially for the Ruiné sampling site (Table 2), and the use of inappropriate R_{scal}. If we consider the R_{scorr}, we may obtain a better concordance between the POCIS estimates and the reference values. However, we observed inaccurate DIA estimates, especially for the Ruiné stream (Figure 4b). This inaccuracy was probably due to matrix effects since analysis of this compound is more impacted by ion suppression than the other test chemicals (Table 2). In some cases, corrections of severe matrix effects will probably necessitate multipoint standard additions. We found that the DIA-*d*5 response was dramatically enhanced in field samples, especially for the POCIS immersed in the Ruiné stream (Table 2). Such signal enhancements may be correlated with the organic matter content since the highest DOC and TOC values were observed for this site. These matrix effects likely reduce the accuracy of the PRC correction and thus the precision as shown by high standard deviations (Figure 4c).

The PRC concept was validated for several triazines in this study. Although, positive evidence is also presented for the phenylurea diuron (Figure 4 a), the applicability of PRCs such as DIA-*d*5 to other classes of chemicals beyond triazines has to be tested and validated in future research. These results also indicated that additional laboratory DIA-*d*5-PRC studies with greater temporal resolution and duration must be carried out to demonstrate first-order isotropic exchange. Furthermore, the analytical problems inherent to the electrospray ionization must be overcome. In fact, the use of HPLC-ESI-MS/MS techniques is compulsory since the GC−MS analyses

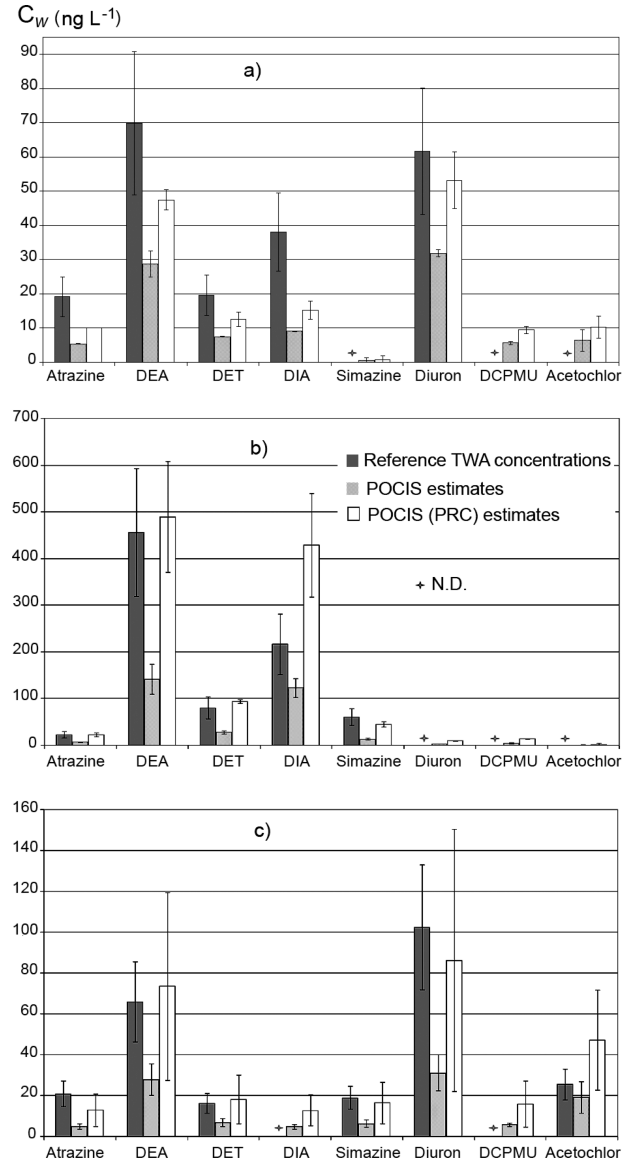

FIGURE 4. In situ 14-day TWA concentrations estimated with either an automatic sampler (reference), or POCIS triplicates with or without PRC corrections. (a) Charente from April 28th to May 13th 2008, (b) Ruiné from April 28th to May 13th 2008, and (c) Charente from May 13th to May 26th 2008.

of some herbicides (e.g., phenylureas) are delicate (*31*). The results of this work indicate that, in some cases, one-point standard additions may be carried out for the evaluation of the matrix effects. Finally, ongoing research at our laboratory is focusing on either cleanup or dilution of POCIS extract to further improve the quantitation of polar herbicides.

Acknowledgments

We are grateful to M. Bonnet, M. Boudigues, B. Delest, B. Mechin, and C. Obeidy for their participation to this work. We also thank the AEAG (Agence de l'Eau Adour-Garonne) and the ONEMA (Office National de l'Eau et des Milieux Aquatiques) for the financial support.

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ES902256M