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Calibration and field application of an innovative passive sampler for monitoring groundwater quality

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Abstract

This study describes the development of a novel Empore™ disk-based passive sampler specially adapted to groundwater monitoring. The sampler was calibrated in the laboratory using conditions that corresponded to groundwater (i.e. matrix medium, water temperature, flow rate and water flow across the disks). The retention and elution performance for sixteen semi-polar and polar pollutants on the Empore™ disk (47 mm diameter, SDB-XC) was evaluated. Recoveries were ~ 80% for the majority of compounds. Sampler uptake kinetics were measured over fourteen days at three concentrations (10, 100 and 500 ng L^{-1}) and the sampling rate (R_S) calculated for four compounds. There was no influence of concentration of the test analyte on the uptake profile; with mean R_S varying between 0.018 ± 0.007 L day^{-1} and 0.047 ± 0.001 L day^{-1}. Passive samplers were deployed in twelve characterized groundwater wells near Lyon (France). Atrazine, atrazine-desethyl and diuron were the main pollutants found with a maximum time-weighted concentration of 61, 62and 127 ng L^{-1} respectively.

Keywords: Emerging polar pollutant, groundwater, passive sampling, uptake kinetic

1. Introduction

Global demand for water (i.e. for agriculture, drinking water, and industrial uses) is constantly growing and water supplies are relying increasingly on groundwater (GW) sources [1]. In some cases, drinking water is pumped from GW aquifers, even from areas known to be impacted by urban and/or agricultural activities. Therefore, monitoring the quality of GW has become a necessity in many parts of the world.

Over the past decade many European monitoring studies (based on spot (bottle or grab) water sampling procedures) have investigated the occurrence of organic pollutants (e.g. hormones, pesticides, pharmaceuticals, personal care products, plasticizers, polyaromatic hydrocarbons and their environmental transformation products (TPs)) in GW [1–5]. In France and in French overseas departments, the most frequently detected pesticides and pharmaceuticals in GW were atrazine and its TPs with concentrations up to 500 ng L^{-1} and acetaminophen and carbamazepine with concentrations up to 100 ng L^{-1} [2–4]. Larger scale GW studies conducted in several countries in Europe found 2,6-dichlorobenzamide (BAM), boscalid, caffeine, and N,N-diethyl-meta-toluamide (DEET) were among the most frequently detected compounds in GW with maximum concentrations between several hundred of ng L^{-1} to several µg L^{-1} [5,6]. Hence there is a growing interest to have a reliable and representative method of quantification for such semi-polar and polar contaminants in GW. Although spot sampling monitoring procedures are commonly used, this method does not provide data on the average concentration of pollutants in aquatic systems as it does not integrate pollution events between two given sampling periods. Furthermore, pollutants in GW can be present at concentrations below limits of quantification (low ng L^{-1} to pg L^{-1}) of analytical methods. This makes their detection difficult when using low volume (e.g. 0.5-1.0 L) spot sampling methods. Passive samplers deployed in water column are potentially able to overcome these limitations as analytes accumulate on a receiving phase over several days or weeks. These

device can yield time-weighted average (TWA) concentrations over their deployment period [7] and the degree of analyte pre-concentration allows for an increase overall analytical sensitivity of the procedure.

Four designs of passive samplers are frequently used to monitor semi-polar and polar pollutants in water namely: organic-diffusive gradient in thin film (o-DGT), polar organic chemical integrative samplers (POCIS), devices with granular activated carbon receiving phases [8], and Empore™ disk (ED)-based samplers such as the Chemcatcher® [7,9]. o-DGT is generally composed of a limiting diffusion membrane, a thick diffusion hydrogel layer and a receiving phase. With this type of sampler, the uptake of analytes is independent of hydrodynamic conditions [10]. However, although it is a promising tool, to the best of our knowledge no study has reported the use of o-DGT in groundwater. POCIS consists of a loose receiving phase solid sorbent held between two limiting diffusion membranes, that are compressed between two stainless steel 'o' rings. Four studies reported the use of POCIS to sequester pollutants in GW [11–14]. Based on the use of hydrophilic-lipophilic balance (HLB) solid-phase sorbent, POCIS can sequester molecules covering a large range of polarity [9]. However, the loose sorbent can move during deployment and this can lead to non-reproducible data as sampler's active sampling surface area can differ over time [7]. Activated carbon passive samplers use a granular material held in stainless steel mesh pouches that are fixed to a thick wire. Three studies used of such devices to assess contamination by organic compounds in GW [8,15,16]. However, only qualitative results were obtained, and further research is needed in order to achieve quantitative results using such a device.

ED passive samplers such as Chemcatcher® are composed of a receiving phase that can in some instances be covered by a thin diffusion limiting membrane. In the Chemcatcher®, EDs (47 mm) are held in place by a screw together polytetrafluoroethylene (PTFE) housing which (~7.0 cm in diameter). However, this type of design does not easily

allow for a deployment in GW as the internal diameter of the well bore-holes (typically ~5.5 cm diameter) is smaller than the PTFE housing. This probably explains why, to the best of our knowledge, only two studies dealt with the assessment of GW contamination by the ED passive sampler.

The first studied five different passive samplers, including the ED (with styrenedivinylbenzene-reversed-phase sulfonated (SDB-RPS) sorbent) sampler, and concluded that they were suitable to characterise organic pollutants in an aquifer system in Australia. But the precise sampler design used in this work was not mentioned [17]. In the second study, SDB-RPS EDs, fixed around a glass bottle with three cable ties, were found to be suitable for detecting active pharmaceutical ingredients in GW in Finland [18]. In these two studies sampling rates were determined in the laboratory for surface water conditions and, only in the case of the first study, were these adjusted for flow rate using a passive flow monitor [17]. However, as GW conditions (e.g. biofouling, water flow rate and water temperature) differ significantly from surface water, the calculated concentrations of the pollutants present may not be accurate. As a consequence, it appears necessary to develop an ED passive sampler design specially adapted to GW monitoring, and to calibrate the device in conditions that correspond typically to GW. To the best of our knowledge, no study deals with such a calibration of a passive sampler in the literature. Hence the objectives of this study were to:

(i) determine the sampling (uptake) rates of semi-polar and polar pollutants using a laboratory calibration experiment performed in environmental conditions as found in GW.

(ii) assess the influence of aqueous concentration of analyte on the uptake behaviour.

(iii) investigate the contamination by semi-polar and polar pesticides and pharmaceuticals in urban GW aquifers.

In order to fulfil these objectives, we first performed a laboratory calibration experiment in order to determine sampler uptake rates. Then a field study was undertaken in twelve GW wells, presenting contrasting physico-chemical conditions, which allowed for the measurement of 16 pesticides and pharmaceuticals.

2. Materials and Methods

2.1. Chemicals.

HPLC-MS grade acetone, methanol (MeOH) and formic acid used in the preparation of the HPLC mobile phases, were from Sigma-Aldrich (Saint-Quentin, Fallavier, France). Compounds selected for the study were considered to be ecotoxicologically relevant according to the literature [19–23] and were detected in GW in a previous study [24]. Atrazine, 2,6-dichlorobenzamide (BAM), bromacil, carbamazepine, carbendazim, desethyl-atrazine (DEA), N,N-diethyl-meta-toluamide (DEET), diclofenac, diuron, fluopyram, hexazinone, imidacloprid, lamotrigine, metolachlor, simazine and sulfamethoxazole were purchased from Sigma-Aldrich. The internal standards atrazine-D_5, carbendazim-D_4, diclofenac-D_4 and isoproturon-D_3 were from CDN Isotopes (Pointe-Claire, Quebec, Canada). Sulfamethoxazole-D_4 was from Toronto Research Chemicals (North York, Canada) and simazine-D_{10} was from HPC Standard (Cunnersdorf, Germany). The purity of all standards was higher than 98%. Individual stock solutions were prepared at concentrations of 1 mg mL^{-1} in MeOH or pure water depending of the solubility of the compound. Working solutions and mixtures were prepared by dilution of stock solutions in MeOH. For the preparation of synthetic GW (SGW), calcium sulfate dihydrate ($CaSO_4.2H_2O$) and magnesium sulfate heptahydrate ($MgSO_4.7H_2O$) both from Merck (Darmstadt, Germany) and potassium chloride

(KCl) and sodium bicarbonate ($NaHCO_3$) both from Sigma-Aldrich were used. Pure water (18.2 MΩ quality) was obtained from a MilliQ device (Millipore, Saint-Quentin-en-Yvelines, France).

Polystyrene divinylbenzene (SDB-XC) Empore™ EDs (47 mm diameter, 12 µm particle size, 0.5 mm thick) were purchased from 3M (Neuss, Germany). Deployment rigs (holding nine individual EDs) designed to fit into GW well dimensions were from the University of Portsmouth (Portsmouth, UK) (see Figure S1) (further details of their construction are given in Pinasseau et al. [24]).

2.2. Analytical methods

2.2.1. Preparation and extraction of SDB-XC disks

SDB-XC disks were cleaned and conditioned by soaking in MeOH overnight, and then washed in water (5 min) prior to placing them on deployment rigs. Nine EDs were placed per rig. After deployment EDs were extracted individually on a tube rotator (20 min) using 10 mL of acetone/MeOH (50/50; *v/v*). Triplicate extracts from three EDs were pooled and then evaporated to dryness under a gentle stream of nitrogen and stored at -20°C until analysis. Finally, samples were reconstituted in 500 µL of water/MeOH (95/5; *v/v*) and diluted 30 times prior to instrumental analysis.

2.2.2 High-pressure liquid chromatography–tandem mass spectrometry (HPLC-MS/MS) analysis

All samples were analyzed using an Agilent Series 1200 HPLC system (Agilent Technologies, Massy, France) equipped with a binary pump coupled to a triple quadrupole mass spectrometer (5500 QTrap, AB Sciex, Les Ulis, France) with an electrospray ion (ESI) source working in positive ionization mode. Chromatographic separation was carried out

using a Poroshell 120 EC-C_{18} column (2.1 × 50 mm, 2.7 µm particle size) (Agilent Technologies) maintained at 30°C; the injection volume was 20 µL. The mobile phases consisted of: (A) water and (B) MeOH with 0.1% formic acid in both phases. The flow rate was 0.5 mL/min. The elution gradient started with 5% of (B), gradually increasing to 70% (B) for the next 6 min then increasing to 100% (B) for 1 min. Then the initial conditions (5% B, 95% A) were restored within 0.1 min to re-equilibrate the column for the next injection. MS detection was carried out in the multiple reaction monitoring (MRM) mode. Two MRM transitions were monitored for quantitation and confirmation purposes (see Table S1). No pharmaceuticals or pesticides were detected in solvent and procedural blanks. Method performance data are given in Table S2.

2.3.Recovery studies

In order to determine analytical recoveries from the EDs, a SGW was prepared by dissolution of appropriate amount of $CaSO_4.2H_2O$ (60 mg L^{-1}), $MgSO_4.7H_2O$ (60 mg L^{-1}), $NaHCO_3$ (96 mg L^{-1}) and KCl (4 mg L^{-1}) in deionized water in order to get a conductivity ~ 300 µS, a water hardness ~ 90 mg L^{-1} of $CaCO_3$, an alkalinity ~ 65 mg L^{-1} of $CaCO_3$ and a pH ~ 7.5 (US EPA, 1991) [25]. The SGW was spiked at 10 ng L^{-1}, 100 ng L^{-1} and 500 ng L^{-1} with a MeOH-mixture of the 16 compounds listed above. A 30 mL aliquot (n = 3) of each spiked solution was filtered through the previously conditioned ED using a 47 mm glass vacuum filter holder. EDs were then extracted as described above and both extracts and eluted filtrate were analysed in order to evaluate the retention and the elution performance of the ED for each analyte.

2.4. Calibration experiments

2.4.1. Experimental set up

Atrazine, hexazinone, metolachlor and sulfamethoxazole were selected for the laboratory calibration experiment as they were representative of the physico-chemical properties of the targeted 16 compounds (see Table S3). A microcosm experiment was performed using sealable columns (24 cm high, 10 cm diameter, 1.9 L volume) made from methacrylate (Figures 1 and S2). A peristaltic pump with Tygon tubing (2.79 mm internal diameter) ensured a constant analyte concentration by continuous renewal of SGW that was spiked with a MeOH-mixture of atrazine, hexazinone, metolachlor and sulfamethoxazole. During the experiment the SGW stock was stored in a 150 L high-density polyethylene tank.

According to literature (BURGEAP 2001) [26,27], glacio-fluvial sediments of the aquifer of Eastern Lyon are highly permeable (10^{-3} to 10^{-2} m s^{-1}) and the slope of GW table is on average 2‰, leading to GW flow rate of around 1 m day^{-1}. To fit with this condition, a flow rate of 5.9 mL min^{-1} was applied in each column with a diameter of 10 cm to obtain a Darcy velocity of 1.08 m day^{-1} in our experimental calibration system.

Experiments took place in the dark with room temperature maintained to 16°C in order to mimic field conditions (average GW temperature of 15°C) [28]. We used a set of seven columns: one column control (without rig) and one column for each of the six exposure times (1, 3, 6, 8, 10 and 14 days). No adsorption effects were observed on either the columns or the tubing during 14 days, as assessed before the calibration started. At the beginning of the calibration, six rigs were submerged in columns, one for each tested exposure time. One rig was sampled at 1, 3, 6, 8, 10 and 14 days of exposure and EDs were extracted and analysed as described above. The experiment was undertaken at three test concentrations: 10 ng L^{-1}, 100 ng L^{-1} and 500 ng L^{-1}. Concentrations were chosen according to the GW quality standard of 100 ng L^{-1} set in the European Union (EU) for individual pesticides and TPs and 500 ng L^{-1} for total concentration of pesticides and TPs in GW (2006/118/EC) [29]. For renewal, freshly prepared SGW was spiked with a MeOH-mixture of atrazine, hexazinone, metolachlor and

sulfamethoxazole and left in the fridge to cool to 16°C and equilibrate before being pumped from the 150 L tank. Concentrations in the tank and at the outlet of the control column were analyzed at each sampling day and at each SGW renewal (Table S4). Temperature and flow rate were controlled during the experiment. Between experiments, the entire system was left to equilibrate.

2.4.2. Uptake kinetic calculations

The theory of the uptake of chemicals by a passive sampler has been described previously [30,31]. The accumulation of analytes in the ED follows a first-order kinetic model. Between the start of exposure and the half-time to equilibrium, the uptake of an analyte is linear and can be described using eq 1:

$$M_S(t) = C_W R_S t \quad (1)$$

where $M_S(t)$ is the mass (ng) of analyte accumulated in the ED after exposure time t (day), C_W is the concentration (ng L^{-1}) of an analyte in the GW and R_S is the sampling rate (L day^{-1}) and represents the volume of water extracted by a sampler per unit of time. During a calibration experiment, R_S can be determined from the slope of the regression between the mass of analyte accumulated against the time of exposure. Once R_S is known, C_W, which corresponds to the TWA concentration during a field deployment, can be calculated.

2.5. Field study

Field trials were undertaken in the eastern metropolitan area of Lyon (France) using twelve GW wells located in sites monitored in the framework of the field observatory in urban hydrology (OTHU, Marmonier et al. [19], Pinasseau et al. [24] and Voisin et al. [32]). By selecting monitored wells, we were confident that water chemistry in the wells did not

differ from that of GW in the aquifer [27,32]. A total of twelve ED rigs were used (one rig per well) and deployed for ten days between 26th of October - 5th of November, 2018. Water conductance and temperature (LTC Levelogger® Junior, Solinst, Canada), dissolved oxygen (HOBO® U26, Onset, USA) and pH were measured during the deployment period. Co-ordinates of the twelve wells, well depths and mean physico-chemical values measured during the deployment period are given in Table S5.

3. Results and Discussion

3.1. Uptake of compounds on a SDB-XC disk

3.1.1. Empore™ disk performance and recoveries

Due to their ability to retain a large range of compounds with differing properties, two of the most commonly used EDs are SDB-RPS and SDB-XC. Our previous study [24] showed a similar performance of these two solid-phase sorbents for semi-polar and polar compounds, but our preliminary experiments showed slightly better and more repeatable recoveries for SDB-XC (data not shown). Consequently, SDB-XC was chosen for this investigation. No polyethersulfone (PES) limiting diffusion membrane was used as is normal in the conventional Chemcatcher® passive sampler. Hence, this allowed for decreasing analytical detection limits as diffusional uptakes of analytes into the ED increased. In addition, there was no need to slow down the sampling process by fitting a PES limiting diffusion membrane, as GW flow velocities are low. Finally, in GW there are few or no biofouling issues, so that protection (as used in surface water investigations) of the ED was not necessary.

In order to evaluate the retention and the elution performance of the EDs for each of the 16 pollutants, 30 mL of SGW (spiked at 10 ng L^{-1}, 100 ng L^{-1} and 500 ng L^{-1}) was filtered through the ED as described in Materials and Methods section. Each experiment was conducted three times. An aliquot of eluted filtrate was analysed in order to estimate the

percentage retention of each analyte. The totality of each analyte was retained on the ED, except sulfamethoxazole for which the retention was ~ 98% (i.e. ~ 2% was found in the eluted filtrate). For two compounds (bromacil and BAM), recoveries increase with concentration (Table 1). On the opposite, for six compounds (diclofenac, hexazinone, DEA, simazine, carbendazim and diuron), recoveries decrease as concentration increases. For these compounds, breakthrough may take place as found by D'Archivio et al. [36]. Increases or decreases in recoveries do not seem to be related to polarity or molecule size. Finally, for the remaining eight compounds, no upward or downward trend is observed as a function of concentration.

When considering the overall mean recoveries, more than half of the compounds had a recovery above 80%. Three had a recovery above 60% and three (fluopyram, metholachlor and sulfamethoxazole) between 42 and 53% (Table 1). Only a few studies reported the evaluation of the retention performance of EDs. Sánchez-Bayo and Hyne [33] found that SDB-XC EDs achieved 100% retention for the five neonicotinoids they studied; including imidacloprid, for which we found a similar result. In another study using the same EDs, retention for three highly polar herbicides ranged between 20-95% [34]. Furthermore, our recoveries for atrazine, diuron, metolachlor and simazine from SDB-XC disk were comparable to the ones calculated in another study (i.e. 82% ± 1, 82% ± 1, 83% ± 1, 80% ± 2 respectively with 5 mL acetone then 5 mL MeOH used as solvent elution) [35].

No trend with polarity (i.e. log D_{ow}) was observed (Table 1), except for the most hydrophilic and hydrophobic compounds that exhibited lower recoveries (52.6 ± 20.5 for sulfamethoxazole and 41.9 ± 4.3 and 51.2 ± 7.4 for metolachlor and fluopyram respectively). Therefore, in accordance with the findings of Charriau et al. [37], SDB-XC disks are generally suitable for the sequestration of compounds with log D_{ow} between ~ 1 to 3, which was the case for the majority of the compounds selected in this study.

3.1.2. Uptake kinetics at different concentrations

In order to evaluate the uptake behavior of the selected pollutants, as well as the influence of analyte concentration, a calibration experiment was performed in conditions similar to those found in GW (see Materials and Methods section). The uptake test was undertaken for atrazine, hexazinone, metolachlor and sulfamethoxazole at 10 ng L^{-1}, 100 ng L^{-1} and 500 ng L^{-1} and results are shown in Figure 2. It was observed that the linear uptake time window decreases with the log D_{ow} of the molecule. Indeed, integrative sampling windows were up to 1 and 10 days for the two most polar compounds, sulfamethoxazole and hexazinone respectively, whereas the uptake was still linear at 14 days for atrazine and metolachlor. In previous studies, integrative sampling time windows for SDB-XC disks (but covered with a PES membrane) were found to be greater than 14 days for atrazine and hexazinone with water flow rates of at least 13.5 cm s^{-1} [38], and 21 days for atrazine and metolachlor with flow rates of 0.4 cm s^{-1} [35]. Vermeirssen et al. [39] found shorter time windows of up to 6 days for atrazine and sulfamethoxazole with water flow rates of 13.0 cm s^{-1}. However, it is difficult to compare calibration data from different authors as experiments were performed using different exposure designs, which induces different hydrodynamic conditions. In our case, data indicated that the linear sampling time window was up to 10 days for the majority of the selected compounds and in conditions close to those found on the GW field sites.

With regard to the mass of analyte accumulated on the ED, hexazinone and atrazine showed similar uptake behavior with a maximum accumulated mass of about 320 ng $disk^{-1}$ (Figure 2). Performance of the ED was lower for the two other compounds with a maximum accumulated mass of about 30 and 150 ng $disk^{-1}$ for sulfamethoxazole and metolachlor respectively. Therefore, these results confirm those found in the previous section concerning

the analytical recoveries, i.e. the ED is more suitable for compounds with log D_{ow} between ~ 1 and 3.

Our results suggested that there was no influence of concentration of analyte on the uptake profile (Figure 2). Linear sampling time windows (i.e. 1 day for sulfamethoxazole, 10 days for hexazinone, and 14 days for atrazine and metolachlor) were the same for all three concentrations, based on the profile of their uptake curves. These results were in accordance with those found in previous studies [33,35].

3.1.3. Calculated sampling rates

In order to determine the TWA concentration (C_W) of the analytes, it was necessary to calculate the sampling rate (R_S) as described in eq 1. R_S is calculated from the slope of the regression between the mass of analyte accumulated against the time of exposure (Figure 2). As a result, we found R_S varied between 0.012 ± 0.001 L day^{-1} for metolachlor at 500 ng L^{-1} and 0.048 ± 0.001 L day^{-1} for hexazinone at 100 ng L^{-1}; with mean R_S of 0.026 ± 0.003, 0.047 ± 0.001, 0.035 ± 0.003, 0.018 ± 0.007 L day^{-1} for sulfamethoxazole, hexazinone, atrazine and metolachlor, respectively (Table 2). R_S were slightly lower for sulfamethoxazole and metolachlor, for which the SDB-XC disk gave lower recoveries than for the two other compounds.

The main differences between our experimental sampling rates and extant literature concerned the water flow rate, the water temperature, the experimental calibration set up and the passive sampler geometry. Concerning water flow rates, it is well known that the higher the flow rate, the higher the R_S [31,39–42]. Therefore, our calculated R_S were much lower than those found in other studies probably because our experiment was conducted with a flow velocity corresponding to GW flow. This is much lower than those measured in river water

(i.e. a few mm s^{-1} for GW against several tens cm s^{-1} for river water). Similarly, the higher the water temperature, the higher the sampling rate [31,43,44]. In our case, the water temperature set for the experiment was slightly lower than those generally found in the literature (i.e. 16 °C against an average temperature of 20 °C) and this could lead to a lower R_S. Furthermore, the configuration of the experimental calibration set up plays a major role in the uptake of the analyte. Indeed, it was already shown that the design of the experimental set up leads to significant differences in the uptakes [45]. Vermeirssen et al. [46] found difference factors of up to almost four in the values of R_S obtained between calibration experiments conducted in a river water channel and in a circular tank. Hence, the calibration experiment should be designed to be the most relevant to the appertaining field conditions. With this in mind, we used columns for the laboratory calibration experiment that were similar to GW wells found in the field. Finally, sampler geometry has an impact on the uptake [45,47]. Further comparison of our sampling rate data with that in the literature was difficult as our novel sampler was especially designed for GW monitoring and no similar designs have been described previously.

To the best of our knowledge, no other study aimed at determining R_S used an experimental rig that simulated GW conditions. Six other studies measured R_S for semi-polar and polar pesticides and pharmaceuticals using a SDB-XC disk [33,35,38,39,48,49]. Calibration experiments were conducted with tap water [33,35,38,48] or surface water [39,49] (i.e. streams and treated sewage effluents), with water temperature varying between 14 and 27 °C. Flow-through systems (i.e. tanks) were mainly used with samplers supported on carousel devices [38,48] or an artificial channel replicating an outdoor stream [39,49]. Flow rates were much higher than the one in our experiment set up (i.e. from 0.4 to 40.0 cm s^{-1} against 0.0001 cm s^{-1}). Accordingly, R_S were also generally higher than in our study. Indeed, with a flow rate of 13.5 cm s^{-1}, Gunold et al. [38] found R_S varied from 0.120 to 0.440 L day^{-1} with 0.260 and

0.280 L day^{-1} for hexazinone and atrazine respectively. With a flow rate of 13.0 cm s^{-1}, Vermeirssen et al. [39] found R_S from 0.080 to 1.120 L day^{-1} with 0.080 and 0.520 L day^{-1} for sulfamethoxazole and atrazine respectively. Sánchez-Bayo et Hyne. [33] and Schäfer et al. [49] calculated R_S of the same order of magnitude as ours with average R_S of 0.010 and 0.045 L day^{-1} respectively. Tran et al. [35] also found R_S from 0.021 to 0.026 L day^{-1} with 0.024 and 0.021 L day^{-1} for atrazine and metolachlor respectively; but with an ED covered by a PES diffusion limiting membrane and a water flow rate of 0.4 cm s^{-1}.

Our study showed that no trend in R_S was seen with the polarity or physico-chemical properties of the analytes; this was already discussed in previous studies using different sorbents [50,51]. This was not surprising as it was recently shown that the overall uptake behavior is controlled by multiple other factors such as molecular diffusion, lag-times and equilibrating behavior [52]. Furthermore, our results showed no influence of the concentration of analyte on R_S, as found in other studies [33,35]. Therefore, as standard deviations for Rs between the three concentrations were on average no more than 15% of the Rs value (Table 2), the overall mean R_S was used to determine C_W in the subsequent field trials.

3.1.4. Calculated method quantification limit

Method quantification limits (MQL) were calculated from the calibration experiment at t = 10 days. The regression curve between the signal-to-noise (S/N) ratio of the extracts against the concentration of pollutant in SGW (10, 100 or 500 ng L^{-1}) was established. With a S/N ratio of 10, the calculated MQL were 0.13, 0.03, 0.17 and 1.35 ng L^{-1} for atrazine, hexazinone, metolachlor and sulfamethoxazole respectively. When comparing IQL (Table S2) and MQL, it appears that the applied passive sampling methodology allows a gain of sensitivity of at least 14 (14, 156, 85 and 14 for atrazine, hexazinone, metolachlor and

sulfamethoxazole respectively). A similar gain of sensitivity using the passive sampler approach was also found in other studies [50,51].

3.2. Semi-quantitative determination of emerging pollutants in groundwater

To determine TWA concentrations (C_W), the extrapolation of the four R_S values to the 16 other compounds in the test set was made on the basis of retention times, log D_{ow}, and chemical structures. We assumed that compounds with similar physico-chemical properties, and in particular with similar behavior on a reversed-phase chromatographic columns (i.e. retention time) would exhibit similar uptake behavior on the ED during the field trial. Consequently, R_S of hexazinone was applied to BAM, bromacil, carbendazim, imidacloprid and lamotrigine; R_S of atrazine was applied to its metabolite and same class compounds, i.e. DEA and simazine respectively, as well as carbamazepine and DEET; and R_S of metolachlor was applied to diclofenac, diuron and fluopyram. R_S of sulfamethoxazole was not applied to any other compound as its integrative sampling window was found to be up to one day while rigs were deployed for ten days. Moreover, as for sulfamethoxazole, C_W of the most polar compounds (e.g. imidacloprid) must be considered with caution as their integrative sampling windows are probably less than 10 days. Therefore, C_W values determined for sulfamethoxazole and imidacloprid should be considered as rough orders of magnitude only.

One of the issues concerning the HPLC-MS analysis of environmental extracts is matrix effects. Matrix suppressions, or sometimes enhancements, were often observed during analysis of samples by HPLC-MS/MS [7,39,53]. Therefore, we diluted samples 30 times before analysis in order to minimize matrix effects. In addition, six internal standards (Table S1) were also added to correct for any matrix effects and to help increase the robustness of the method. After such a dilution, matrix suppressions in the ED blank and GW extracts were all

below 30% for the six internal standards, except for diclofenac-D_4 which exhibited a matrix suppression of 36% in GW (Figure S3).

After retrieval of the twelve deployment rigs (six sites, with two GW sampling points per site and analysis of the GW extracts, C_W were determined and average and maximum values are given in Table 3.

All pollutants were found with a global detection frequency above 58% and five of them were detected in 100% of cases (atrazine, carbendazim, DEA, DEET and diuron). Frequency of detection of pollutants with C_W > MQL was lower for several compounds such as fluopyram and and sulfamethoxazole for which percentage decreases from 83 to 67% and from 75 to 25% respectively. It means that these compounds are frequently detected, but at very low concentrations. Diuron, DEA and atrazine exhibited the three highest maximum C_W with 127, 62, and 601 ng L^{-1} respectively, and were also found in 100% of cases. Diuron (one sample) was the only pollutant that exceeded the European GW quality standard of 100 ng L^{-1}. DEA, simazine, diuron, atrazine and DEET were the five pollutants with the highest median C_W with 21, 15, 14, 13 and 12 ng L^{-1} respectively (Table 3). Similar results were found previously during a screening of 411 emerging pollutants undertaken through two sampling campaigns at 494 GW sites in France [2]. Atrazine and atrazine TPs were the most commonly detected pesticides with spot sample concentrations up to 500 ng L^{-1} and carbamazepine was found to be one of the most frequently detected pharmaceuticals with spot sample concentrations up to 100 ng L^{-1}. Two other studies confirmed similar results to ours: one was a regional south-east quarter of France screening program where 70 GW wells were assessed [3]; the other was a screening of 40 GW sampling points of French overseas department [4]. A larger scale study (42 target pollutants, during a survey of 345 GW sites) conducted in France and the United Kingdom found that BAM was the highest pesticide detected, with a

concentration of up to 10 μg L^{-1} [5]. Atrazine, DEA and diuron were among the most frequently detected pesticides in French GWs. In a pan-European investigation (59 pollutants targeted in 164 GW samples) involving 23 countries, DEET and atrazine were most frequently detected with spot sample maximum concentrations of 454 ng L^{-1} and 253 ng L^{-1} respectively [6]. DEA, simazine, carbamazepine, diuron and sulfamethoxazole were also found to be present in many samples. The pesticides, atrazine, metolachlor, simazine and diuron were withdrawn from sale in France in 2003 [54]. However, these persistent pollutants are still widely detected in the environment and found increasingly in GW. The long renewal times of the aquifers [55], which may take years to decades, can partially explain the occurrence of such contaminants in GW even several years after their banning [56]. Furthermore, the high frequency of detection and high concentration of diuron can be explained by the fact that it is constantly released to the environment as it is used in film preservatives [57].

4. Conclusions

This work used a novel ED-based passive sampler that was specially designed to be used in standard sized GW wells. Using such a device has many advantages over the conventional spot water sampling procedures that are used currently in GW monitoring programs across the globe. The use of passive samplers may help in the prioritization of emerging chemicals of concern in ground water; it is recognized that there is an urgent need for such a classification [58].

A simple laboratory set up can be used to calibrate the samplers using a matrix-matched medium and in conditions that replicate those found in GW aquifers. In future, uptake rate (R_S) values for a wider range of compounds of environmental interest need to be obtained to facilitate the measurement of time-weight average concentrations of additional

key pollutants in the GW wells. As increased monitoring of GW wells will be needed in the future, the use of passive samplers represents a viable new monitoring approach for end-users. This, however, will require the development of quality assurance and control procedures, as well as validated guidelines for use of the technology as are available for monitoring pollutants surface waters [59].

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Figure S1. Photographs of ED supports designed specially adapted to GW well dimensions.

Figure S2. Photographs of the experimental set up used for the adsorption experiment.

Figure S3. Matrix suppression of studied pollutants (ordered by retention time); response in ED blank and groundwater extracts after dilution 30 times.

Table S1. Details of HPLC-MS/MS method (pollutants are ordered by retention time).

Table S2. Performance data for the HPLC-MS/MS method.

Table S3. Physico-chemical properties of studied pollutants.

Table S4. Mean concentrations of the four test analytes measured in the exposure tanks and outlet of the control column at each sampling day and at each SGW renewal (n = 17).

Table S5. Co-ordinates of the GW wells, well depths and mean physico-chemical values measured during the sampler deployment period.

Figure S1. Photographs of ED supports designed specially adapted to GW well dimensions.

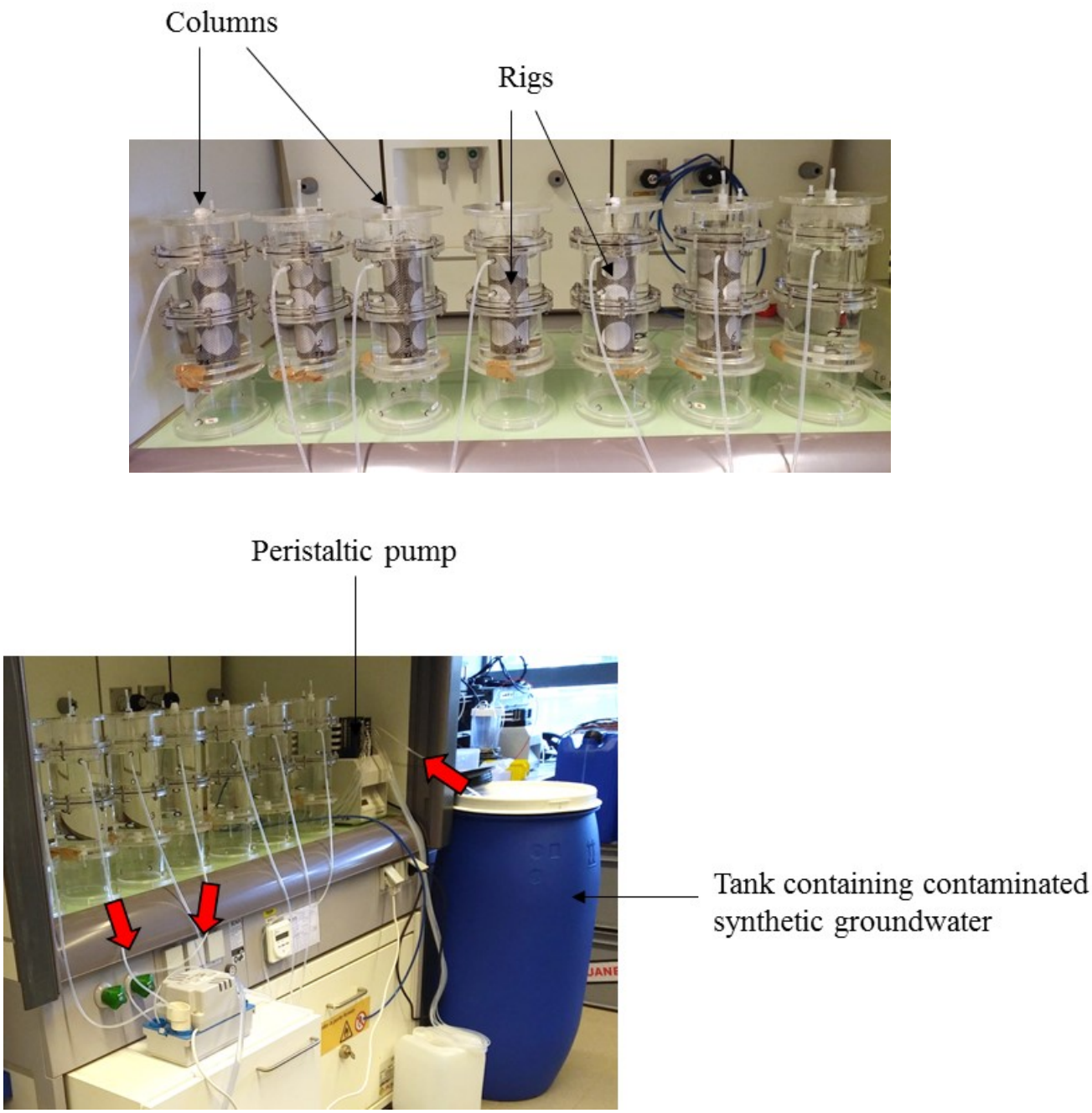

Figure S2. Photographs of the experimental set up used for the adsorption experiment.

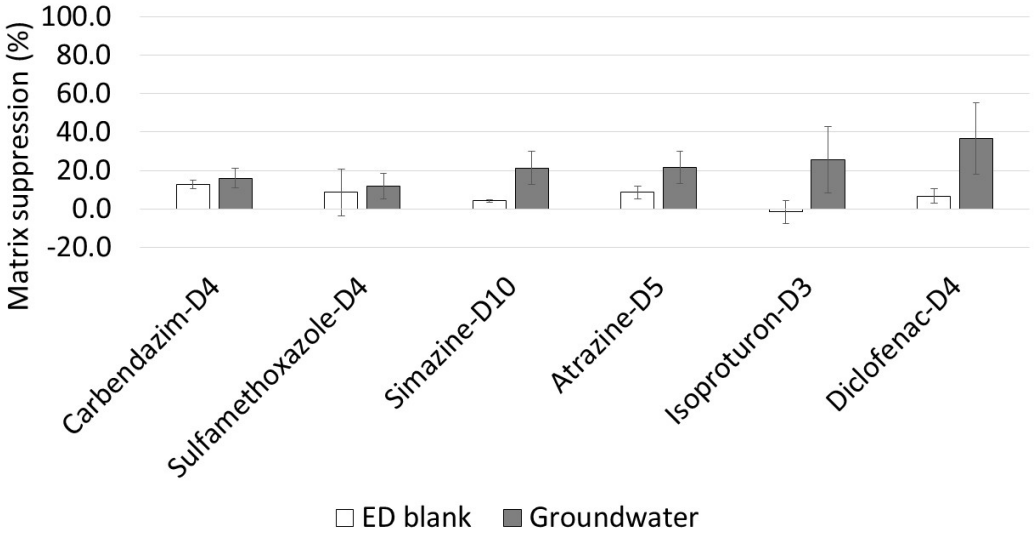

Figure S3. Matrix suppression of studied pollutants (ordered by retention time); response in ED blank and groundwater extracts after dilution 30 times

Table S1. Details of HPLC-MS/MS method (pollutants are ordered by retention time).

Pollutant	R_t (min)	Precursor ion (m/z)	DP (V)	Product ion 1 (m/z)	CE 1 (V)	CXP 1 (V)	Product ion 2 (m/z)	CE 2 (V)	CXP 2 (V)	Ion ration[a]	Corresponding labelled internal standard
BAM	3.1	190.0	76	173.0	27	14	109.0	49	12	2.34 ± 0.12	Sulfamethoxazole-D_4
Carbendazim	3.6	192.1	86	160.0	25	14	132.1	41	12	4.56 ± 0.25	Carbendazim-D_4
Sulfamethoxazole	4.6	254.1	76	156.0	21	12	92.0	35	12	1.02 ± 0.11	Sulfamethoxazole-D_4
Imidacloprid	4.8	256.1	66	209.1	23	20	175.1	27	12	0.97 ± 0.05	Sulfamethoxazole-D_4
DEA	5.3	188.1	86	146.0	25	12	104.0	35	10	3.65 ± 0.17	Atrazine-D_5
Lamotrigine	5.3	256.0	141	211.0	37	18	145.0	53	12	1.44 ± 0.21	Simazine-D_{10}
Bromacil	6.5	261.1	76	205.0	21	16	187.9	39	14	6.04 ± 0.38	Simazine-D_{10}
Simazine	6.5	202.1	106	132.0	27	10	124.1	25	10	1.08 ± 0.05	Simazine-D_{10}
Hexazinone	6.6	253.2	81	171.1	23	12	71.1	41	10	2.93 ± 0.23	Atrazine-D_5
Carbamazepine	7.1	237.1	101	194.1	27	18	179.1	49	14	6.47 ± 0.97	Atrazine-D_5
Atrazine	7.2	216.1	106	174.1	25	12	104.0	39	12	2.96 ± 0.39	Atrazine-D_5
DEET	7.3	192.1	96	119.0	25	12	91.0	41	12	1.45 ± 0.10	Isoproturon-D_3
Diuron	7.5	233.0	81	72.0	23	12	160.0	23	12	15.79 ± 3.35	Isoproturon-D_3
Fluopyram	8.0	397.0	86	208.0	29	14	145.0	73	12	0.91 ± 0.09	Diclofenac-D_4
Metolachlor	8.0	284.1	76	176.2	35	12	252.2	21	18	0.32 ± 0.07	Isoproturon-D_3
Diclofenac	8.1	296.0	66	214.1	27	14	151.1	87	12	4.66 ± 0.54	Diclofenac-D_4
Carbendazim-D_4	3.6	196.1	60	164.2	25	12	-	-	-	-	-

Sulfamethoxazole-D_4	4.6	258.1	66	160.0	23	12	-	-	-	-	-
Simazine-D_{10}	6.5	212.0	66	137.1	29	20	-	-	-	-	-
Atrazine-D_5	7.2	221.1	106	179.1	25	14	-	-	-	-	-
Isoproturon-D_3	7.7	210.1	86	75.1	25	10	-	-	-	-	-
Diclofenac-D_4	8.1	300.0	66	218.1	47	14	-	-	-	-	-

Key: R_t, retention time; DP, declustering potential; CE, collision energy; CXP, collision cell exit potential. Entrance potential = 10 V, source temperature = 550 °C, ion spray = 5500 eV, nebulizing gas = 50 psi, drying gas = 60 psi.

[a]MRM ratio: Product ion 1/Product ion 2 ratio average over the entire calibration range

Table S2. Performance data for the HPLC-MS/MS method.

Pollutant	**IDL**	**IQL**	**RSD (n = 3)**
	(ng L^{-1})	**(ng L^{-1})**	**(%)**
Atrazine	0.5	1.8	9
Hexazinone	1.4	4.7	13
Metolachlor	4.3	14.5	7
Sulfamethoxazole	5.6	14.7	5
BAM	5.2	17.4	6
Bromacil	9.0	30.0	5
Carbamazepine	2.8	9.2	9
Carbendazim	2.4	8.1	8
DEA	1.9	6.3	9
DEET	1.2	3.8	6
Diclofenac	2.9	9.5	7
Diuron	7.1	23.6	3
Fluopyram	1.8	6.1	13
Imidacloprid	13.5	45.1	6
Lamotrigine	9.0	30.0	7
Simazine	1.4	4.6	1

Key: IDL, instrument detection limit; IQL, instrument quantification limit; RSD, relative standard deviation

Table S3. Physico-chemical properties of studied pollutants.

Pollutant	Pollutant class[b]	CAS No.	Molecular formula	Molecular weight (g mol^{-1})	Log D_{ow} (pH = 7.4)[c]	Speciation (pH = 7.4)
Atrazine[a]	Herbicide	1912-24-9	$C_8H_{14}ClN_5$	215.68	2.20	Neutral
BAM	Herbicide TP	2008-58-4	$C_7H_5Cl_2NO$	190.02	2.03	Neutral
Bromacil	Herbicide	314-40-9	$C_9H_{13}BrN_2O_2$	261.12	1.69	Neutral
Carbamazepine	Pharmaceutical	298-46-4	$C_{15}H_{12}N_2O$	236.27	2.77	Neutral
Carbendazim	Fungicide	10605-21-7	$C_9H_9N_3O_2$	191.19	1.80	Neutral
DEA	Herbicide TP	6190-65-4	$C_6H_{10}ClN_5$	187.63	1.54	Neutral
DEET	Insecticide	134-62-3	$C_{12}H_{17}NO$	191.27	2.50	Neutral
Diclofenac	Pharmaceutical	15307-86-5	$C_{14}H_{11}Cl_2NO_2$	296.15	1.10	Anionic
Diuron	Herbicide	330-54-1	$C_9H_{10}Cl_2N_2O$	233.10	2.53	Neutral
Fluopyram	Fungicide	658066-35-4	$C_{16}H_{11}ClF_6N_2O$	396.72	4.23	Neutral
Hexazinone[a]	Herbicide	51235-04-2	$C_{12}H_20N_4O_2$	252.32	1.37	Neutral
Imidacloprid	Insecticide	138261-41-3	$C_9H_{10}ClN_5O_2$	255.66	0.78	Neutral
Lamotrigine	Pharmaceutical	84057-84-1	$C_9H_7Cl_2N_5$	256.09	1.91	Neutral
Metolachlor[a]	Herbicide	51218-45-2	$C_{15}H_{22}ClNO_2$	283.79	3.45	Neutral
Simazine	Herbicide	122-34-9	$C_7H_{12}ClN_5$	201.66	1.78	Neutral
Sulfamethoxazole[a]	Pharmaceutical	723-46-6	$C_{10}H_{11}N_3O_3S$	253.28	0.00	Anionic

[a]Pollutants selected for the calibration experiment
[b]TP: transformation product
[c]As calculated on Chemicalize (https://chemicalize.com)

Table S4. Mean concentrations of the four test analytes measured in the exposure tanks and outlet of the control column at each sampling day and at each SGW renewal (n = 17).

Pollutant	**Uptake experiment (500 ng L^{-1})**	**Uptake experiment (100 ng L^{-1})**	**Uptake experiment (10 ng L^{-1})**
	(ng L^{-1})	**(ng L^{-1})**	**(ng L^{-1})**
Atrazine	485 ± 17	94 ± 10	10 ± 1
Hexazinone	535 ± 39	86 ± 7	8 ± 1
Metolachlor	445 ± 26	104 ± 5	10 ± 2
Sulfamethoxazole	457 ± 24	73 ± 7	7 ± 1

Table S5. Co-ordinates of the GW wells, well depths and mean physico-chemical values measured during the sampler deployment period.

Wells	Co-ordinates	Unsaturated zone thickness (m)	Well depth (m)	Conductivity (µS cm^{-1})	pH	Temp (°C)	DO (mg L^{-1})	N-NO_3^- (mg L^{-1})	N-NH_4^+ (µg L^{-1})	P-PO_4^{3-} (µg L^{-1})	DOC (mg L^{-1})
1	45°39'27.8"N 4°53'42.9"E	1.5	3.6	787	7.7	16	7.04	6.83	105.6	66.3	0.83
2	45°39'34.1"N 4°53'43.1"E	2.2	3.6	914	7.9	16	7.27	6.57	75.5	12.2	0.95
3	45°39'42.5"N 4°56'14.5"E	18.0	28.0	556	7.6	18	8.27	4.73	69.5	8.6	0.86
4	45°39'40.8"N 4°56'19.8"E	18.2	28.0	808	7.5	15	8.16	7.22	56.3	10.4	0.66
5	45°40'29.8"N 4°57'29.9"E	13.4	28.9	503	7.7	15	8.17	3.51	75.2	7.6	0.82
6	45°40'30.8"N 4°57'34.5"E	14.1	28.9	455	7.8	16	8.25	3.08	64.0	7.0	0.97
7	45°42'55.9"N 4°54'56.3"E	3.0	4.8	230	8.1	12	7.74	0.49	66.4	3.7	1.92
8	45°42'55.5"N 4°55'14.0"E	3.3	4.8	302	8.2	11	7.90	0.06	56.9	7.6	2.95
9	45°44'12.2"N 4°57'23.3"E	19	25.0	519	7.7	16	6.72	3.64	37.8	7.7	1.00
10	45°44'13.7"N 4°57'32.1"E	17.8	25.0	708	7.6	15	7.55	9.56	45.2	10.0	1.93
11	45°47'14.2"N 4°52'55.3"E	1.5	4.5	143	8.4	11	7.61	0.18	7.2	21.7	1.61
12	45°46'49.2"N 4°52'06.0"E	2.2	4.5	594	8.1	16	6.43	2.40	60.6	7.3	0.76