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Passive sampling of anionic pesticides using the Diffusive Gradients in Thin films technique (DGT)

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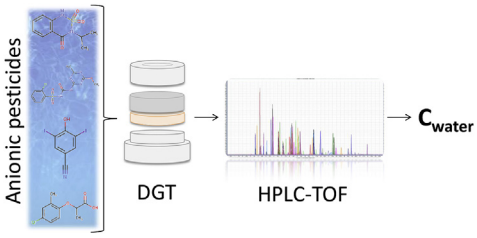
HIGHLIGHTS

- DGT is optimized for anionic pesticides from different chemical groups.
- Polyacrylamide is more suitable than Agarose for diffusive gel.
- HLB-DGT is more suitable than MAX-DGT.
- Successful quantifications are demonstrated in laboratory.
- Successful *in situ* applications are demonstrated in two Rivers.

GRAPHICAL ABSTRACT



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ABSTRACT

DGT passive samplers using Oasis® HLB or Oasis® MAX sorbent were developed for anionic pesticides sampling. They were tested using four model compounds (*i.e.* bentazon, chlorsulfuron, ioxynil and mecoprop). Polyacrylamide diffusive gel was found to be more suitable than agarose gel for most anionic pesticides sampling. An elution procedure was optimized and diffusion coefficients were determined for quantitative use of the samplers. Depending on the DGT configuration used (HLB or MAX), accuracies better than 30% were demonstrated in laboratory for pH from 3 to 8 and ionic strengths from 10^{-2} to 1 M. Combined with the effective binding capacities of samplers (≥9 μg for each pesticide) and limits of quantification of the method (≤13 ng.L^{-1} using Q-TOF detector) monitoring of numerous aquatic systems can be expected. Except for ioxynil, accurate quantifications were demonstrated in laboratory using a spiked natural water for HLB-DGT whereas MAX-DGT did not give satisfactory results. A further *in situ* validation was performed in two rivers and showed identical detection frequency between HLB-DGT and POCIS of anionic pesticides (bentazon and mesotrione) whereas calculated concentrations, although within the same order of magnitude, could differ (<70%). HLB-DGT could therefore constitute an interesting alternative to other passive samplers for the monitoring of several anionic pesticides in aquatic systems but more work is required for quantification of molecules from hydroxybenzonitrile chemical group (ioxynil).

1. Introduction

Passive sampling is gaining interest for monitoring water quality and its use as a complement to spot sampling was recently proposed in the framework of regulatory monitoring programs [1–3]. The main advantage of passive sampling lies in the determination of time-weighted average concentrations of chemicals (TWAC), allowing complementary knowledge on system contamination combined with spot concentrations. In addition, the potential gain in quantification limits can improve detection for some trace pollutants. Among the various passive samplers, POCIS (Polar

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Organic Chemical Integrative Sampler) with Oasis® HLB sorbent is the most commonly used for the study of polar pesticides [4–6]. Environmental parameters (mainly water flow rate) may, however, increase uncertainty of pesticide quantification [7,8]. Indeed, the calculation of TWAC requires the use of sampling rates that were shown to be flow dependant [9–11]. TWAC estimation under different field conditions can therefore be biased by the use of laboratory-derived sampling rates. The PRC (Performance and Reference Compound) approach was developed to overcome this limitation by an *in situ* correction of sampling rates, but it is not validated for ionic pesticides due to anisotropic behavior [7]. Currently, quantification accuracy using POCIS under environmental conditions is assumed to lie between −50% and +100% [3].

The DGT (Diffusive Gradients in Thin films) passive sampler has been used for more than 20 years for sampling inorganic compounds such as trace metals, metalloids or phosphorus [12–15]. This sampler differs from other passive samplers by the incorporation of a diffusive gel layer able to control analyte transfer in the sampler. TWAC estimation using DGT device requires, therefore, only the diffusional characteristics of compounds (*i.e.* diffusion length and diffusion coefficient). The influence of water flow rate on quantification is relatively well documented compared to passive samplers currently used for pesticides (*e.g.* POCIS) [16–18]. Diffusion length in the DGT system is composed of the diffusive gel length and water boundary layer length. Flow rate decrease induce increase in water boundary layer length and subsequent modification of diffusion length. This phenomenon has been shown to alter TWAC estimation only for low flow rates conditions (*i.e* < 10 cm s^{-1}) [19–21]. In a context where the development of new passive samplers for ionic organic compounds is recommended [7], DGT appears to be potentially an interesting tool. Recent developments have adapted DGT to organic compounds by using various binding phases, but currently apply to only a few substances. The first attempt to develop an organic version of DGT was for antibiotics in river [22] and wastewater [23] using an XAD-18 binding layer. Other DGT developments allowed sampling of bisphenols (activated charcoal) [24] and 4-chlorophenol (molecularly imprinted polymer) [25]. Sampling of anionic pesticide using DGT is only poorly addressed. Few years ago, an attempt to sample an anionic pesticide (glyphosate) and its metabolite (aminomethyl phosphonic acid) using titanium dioxide DGT was not robust in synthetic freshwater [26]. Only very recently, DGT based on Oasis® HLB sorbent [27] used in POCIS and Strata-X sorbent [28] were proposed to sample polar organic compounds such as pesticides, pharmaceuticals and personal care products. Challis et al. [27] demonstrated the potential of this technique for an anionic pesticide (2,4-D) but this method was not optimized for such compounds and no field validation was demonstrated for anionic pesticides.

This work aimed at optimising a DGT device for monitoring anionic pesticides. Four anionic herbicides from different chemical groups were chosen as model compounds: bentazon (pKa 3.3; benzothiazinone), chlorsulfuron (pKa 3.4; sulfonylurea), ioxynil (pKa 4.1; hydroxybenzonitrile) and mecoprop (pKa 3.1; aryloxyalkanoïc acids).[1] Oasis® HLB (hydrophilic-lipophilic balanced polymer) and Oasis® MAX (polymer with additional quaternary ammonium functional groups), frequently used for pesticide extraction [29–32], were selected as binding materials. In the present work binding on both sorbents and diffusive gel was studied and an elution procedure was optimized (solvent composition and elution duration). Effective binding capacities and diffusion coefficients were determined for TWAC estimations. The effect of pH and ionic strength was evaluated and a further application of the DGT to spiked natural waters was performed in laboratory. Finally, the developed DGT were validated on field and compared to POCIS passive sampler following *in situ* deployment in two rivers.

[1] pKa values from the Pesticide Properties DataBase (http://sitem.herts.ac.uk/aeru/ppdb/en).

2. Experimental section

2.1. Reagents and general procedures

Ultrapure water (UPW) was produced by a Gradient A10 Milli-Q system from Millipore. Reagents used for HPLC-MS analysis were of HPLC-MS grade (methanol from J.T. Baker, formic acid from Agilent and ammonium formate from Scharlau). Pesticides (bentazone, chlorsulfuron, ioxynil and mecoprop) (>97%) and internal standards (bentazone-d6, MCPA-d3 and metsulfuron-methyl-d3) (>95%) were obtained from Dr. Ehrenstorfer GmbH. Pesticides properties are presented in Table S1. All other reagents were of analytical grade. Oasis® HLB or Oasis® MAX sorbent were purchased from Waters. Laboratory experiments (except analysis, see supplementary material for details) were run at 20 ± 1 °C or, if experiment duration exceeded 24 h, at 5 ± 1 °C to avoid pesticides degradation.

2.2. DGT preparation

Polyacrylamide and agarose diffusive gels were tested. Polyacrylamide (15% acrylamide, 0.3% DGT Research patented cross-linker) and agarose (1,5% agarose) diffusive gels were prepared according to the procedure of Zhang and Davison [33]. Binding gels were prepared with polyacrylamide only. 300 mg of sorbent material (Oasis® HLB or Oasis® MAX) were mixed with 10 mL of a solution containing 15% acrylamide and 0.3% DGT Research patented cross-linker. Then, for HLB and MAX binding gels, respectively 60 or 130 μL of 10% ammonium persulfate solution and 15 or 50 μL of TEMED catalyst were added. Binding gels were immediately cast between two glass plates separated by Teflon® spacers (0.5 mm thickness), placed at 4 °C for 30 min to allow settling of sorbent particles then at 45 °C for about 45 min to complete polymerization. All gels were hydrated in UPW for 24 h with at least five bath renewals and then stored in 10^{-2} M $NaNO_3$ solution at 4 °C before use. After hydration, the average thickness of the polyacrylamide diffusive gels and of the HLB and MAX binding gels were 0.77 (±0.05, n = 19), 0.69 (±0.01, n = 4) and 0.67 mm (±0.01, n = 4), respectively. The DGT system assembly was performed by enclosing a binding gel disc and a polyacrylamide diffusive gel disc inside a piston type molding (DGT Research Ltd.). HLB-DGT and MAX-DGT will refer to DGT equipped with HLB or MAX binding gels, respectively.

2.3. Uptake and desorption of pesticides by diffusive and binding gels

Sorption of anionic pesticides by diffusive gels was investigated to evaluate their suitability for the DGT technique. For this purpose, polyacrylamide or agarose diffusive gels were immersed (n = 3) for 4 h in solution containing 10 μg L^{-1} of each pesticide. A control experiment was performed without diffusive gel. Sorption was estimated according to the difference between initial concentration and concentration measured after 4 h in solution.

To evaluate uptake by binding gels, 24 binding gels (HLB or MAX) were immersed for 12 h at 20 °C in 10 mL of solutions containing a mixture of the four pesticides (50, 100 and 250 μg L^{-1} each in 10^{-2} M $NaNO_3$). Desorption was tested by soaking binding gels