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## Sensitivity improvement of o-DGT for organic micropollutants monitoring in waters: Application to neutral pesticides

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### Abstract

In this study, a larger configuration of the o-DGT, labelled “Large o-DGT” (Lo-DGT), was evaluated to increase its sensitivity. The Lo-DGT presents the same configuration as the conventional o-DGT except for a 4.8-fold increased sampling area (15.2 cm<sup>2</sup>) due to the use of a larger, commercially available, holder (Chemcatcher). The Lo-DGT was evaluated both in laboratory and on the field for the sampling of 24 model neutral pesticides and metabolites that have a large range of log K<sub>ow</sub> (from 0.43 to 3.95) and chemical groups. The elution procedure was adapted to the larger binding gels and gave similar elution factors than those of the o-DGT (elution factors between 0.74 and 0.96). The compounds accumulation behavior in the o-DGT and the Lo-DGT devices were compared at laboratory-scale through simultaneous deployments in a synthetic solution over different durations (4 h to 24 h). The accumulation in the Lo-DGT was consistent with the DGT theory, *i.e.*, linear over time, and the accumulated masses were systematically 4.8-times higher than in the conventional o-DGT. Finally, both devices were compared under field conditions during a conventional 14-days deployment in two rivers with a context of low contamination by pesticides (total neutral pesticides < 0.1 µg L<sup>-1</sup>). In both rivers, the Lo-DGT allowed a higher quantification frequency than the conventional o-DGT, due to its lower LOQ (0.2 to 1.3 ng L<sup>-1</sup> versus 0.8 to 8.1 ng L<sup>-1</sup>). For compounds quantified with both devices, the time-weighted average concentrations were similar. The Lo-DGT therefore appears as reliable as the o-DGT for the monitoring of the tested compounds in waters but with lower LOQ, consequently allowing a better assessment of the water quality.

**Keywords:** *Passive sampling, DGT, Pesticides, Polar organic compounds, Water monitoring*

## 1 Introduction

Over the last years, the use of the Diffusive Gradients in Thin films for monitoring organic micropollutants (o-DGT) in water has considerably grown [1]. Since 2012, the o-DGT devices have been used to sample an extensive range of organic compounds including pesticides, pharmaceuticals, hormones, household and personal care products [2]. Compared to other passive samplers, such as the Polar Organic Chemical Integrative Sampler (POCIS) [3] and the Chemcatcher [4], the advantage of the o-DGT is to be less influenced by the hydrodynamic fluctuations in the water [5]. This results from the addition of a diffusive gel in the o-DGT device that constrains the mass transfer mostly to the diffusion flux within the gel [6]. Indeed, due to its significant thickness (typical 0.8 mm), the diffusive gel limits the contribution of the diffusive boundary layer (DBL) present at the surface of the o-DGT to the total diffusion path. Thus, even if the thickness of the DBL evolves with every fluctuation of the hydrodynamic conditions, its impact on the mass transfer of a compound in the o-DGT is minor, allowing a more reliable conversion of the accumulated mass into exposure concentration. The value of the diffusion coefficient in the gel and the thickness of the gel are thus the only required parameters to accurately calculate the time weighted average water concentration (TWAC) of a compound. The diffusion coefficient of a given compound through the diffusive gel is only temperature-dependent, which can be easily corrected [7]. As a result, compared to other passive samplers, the o-DGT does not require a calibration that matches the targeted deployment conditions, limiting inaccuracies under variable flow conditions.

However, the main drawback of the o-DGT is its lower sensitivity, in particular for environmental concentrations ranging from  $\text{ng L}^{-1}$  (or less) to  $\mu\text{g L}^{-1}$ , as already demonstrated for several antibiotics [8] and anionic pesticides [9]. The longer diffusion path, induced by the diffusive gel, and the lower sampling area (only  $3.14 \text{ cm}^2$  versus  $15.2 \text{ cm}^2$  for Chemcatcher and  $46 \text{ cm}^2$  for POCIS) both contribute to lower sampling rates and consequently to a lower sensitivity. This can represent an issue for water quality monitoring, considering the generally low concentrations of organic compounds. This is even more significant in headwaters [10] that are considered important for natural biodiversity preservation but may be vulnerable to low pesticide contaminations. To increase the analyte concentration in the sampler and therefore improve its sensitivity, the o-DGT could be deployed for longer times (several weeks) but this strategy can favor the development of biofilm on the surface of the sampler and potentially alter the accumulation behavior [11,12] or lead to a degradation of the diffusive gel. According to the DGT model (described by Davison and Zhang [13]), the accumulated mass being directly proportional to the sampling area, an alternative strategy could consist in developing larger o-DGT devices [5].

New designs with increased sampling area have thus been recently proposed, based on a Petri dish [14] or a two-sided device [15] ( $78 \text{ cm}^2$  and  $22.7 \text{ cm}^2$ , respectively). These samplers were calibrated and tested under field conditions but their compliance with DGT theory has not been verified and no comparison to the conventional DGT design is available. Therefore, the impact of modifying the sampling area on the accuracy of the TWAC modelling by the common DGT theory (*i.e.*, simplified diffusion-based equation) is currently unknown. The DGT model usually applied for quantification does not take into consideration the contribution of the DBL nor the lateral diffusion to the diffusion flux, two phenomena that systematically occur during a DGT deployment. Such simplification has been validated for the conventional design of the DGT ( $3.14 \text{ cm}^2$  sampling area) since it has been demonstrated that both phenomena compensate each other [4, 14]. However, this simplification is not necessarily valid for other DGT designs. Although increasing the sampling area will not modify the DBL effect (hydrodynamic issue), the lateral diffusion contribution is likely to be modified. Using a larger area, the lateral flux (proportional to the perimeter) will increase but to a lesser extent than the front flux (proportional to the surface). The resulting lateral diffusion contribution to the global flux should therefore be lower than with a conventional DGT design. Consequently, the compensation between DBL and lateral diffusion contribution could not be valid in larger DGT design, leading to a potential bias in the quantification.

In this study, we propose to evaluate a larger configuration, labelled “Large o-DGT” (Lo-DGT), based on the exact same configuration than the conventional o-DGT but using the commercially available support of the Chemcatcher device. This holder has a sampling area that is 4.8 times higher than the conventional DGT holder (15.2 cm<sup>2</sup> versus 3.14 cm<sup>2</sup>) and is thus expected to improve the sensitivity by a 4.8-factor. The aim of this study was to evaluate the reliability of the enlarged design of the Lo-DGT and its interest for improving water monitoring, particularly in low contamination contexts. The Lo-DGT was evaluated for the sampling of 24 model neutral pesticides and metabolites that cover a wide range of hydrophobicity (log K<sub>ow</sub> from 0.43 to 3.95) and chemical groups. In a first step, the diffusion coefficients were determined and the elution step of the Lo-DGT binding gels was optimized. In a second step, the consistency of the DGT quantification model with the new design was checked. For this purpose, the accumulation behaviors in the Lo-DGT and in the conventional o-DGT devices were simultaneously compared in laboratory. Finally, both devices were compared under field conditions during a deployment in two low-contaminated rivers.

## 2 Experimental section

### 2.1 Chemicals

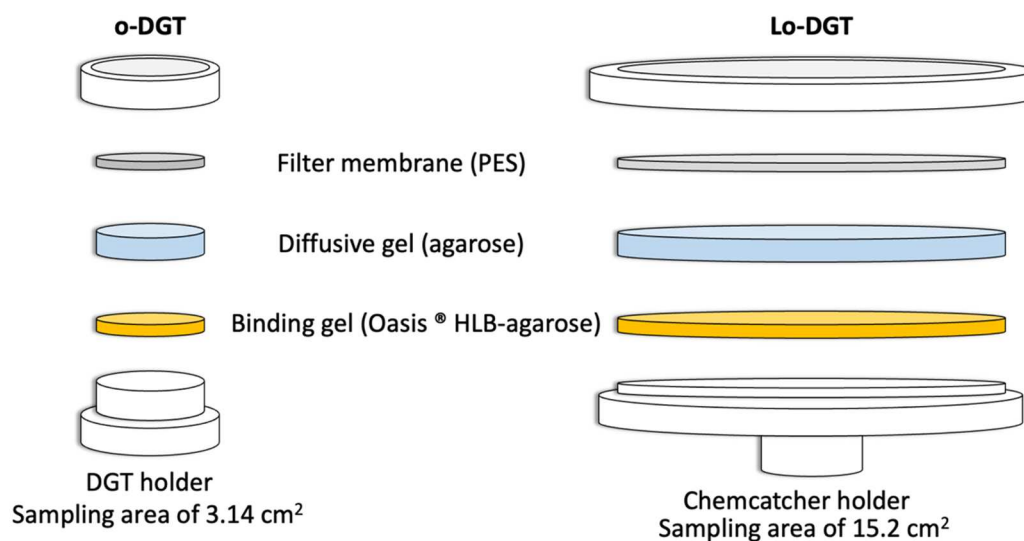
The suppliers of each chemical and material used are indicated in **Table S1**. The ultrapure water (UPW) (resistivity > 18.2 MΩ) was produced by a MilliQ system. The methanol (MeOH) was of LC-MS grade. The 24 studied pesticides and metabolites (high purity > 95%) were the following: Atrazine, Atrazine-deisopropyl (DIA), Atrazine-desethyl (DEA), Carbendazim, Chlortoluron, Cybutryne, Dimethachlor, Dimethenamid, Dimethoate, Diuron, Epoxiconazole, Ethidimuron, Flurochloridone, Flurtamone, Hexazinone, Imidacloprid, Isoproturon, Metazachlor, S-Metolachlor, Propiconazole, Simazine, Tebuconazole, Terbutylazine and Terbutylazine-2-hydroxy. They cover a wide range of hydrophobicity, with log K<sub>ow</sub> between 0.43 and 3.95, and of chemical groups (**Table S2**). Individual pesticide stock solutions at a concentration of 100 mg L<sup>-1</sup> were prepared in MeOH and stored at -18°C. Diluted solutions were prepared daily for each experiment.

### 2.2 o-DGT and Lo-DGT assembly

The DGT samplers were prepared by enclosing a binding gel, a diffusive gel, and a protective membrane in a piston-type holder. The gels were prepared according to Challis et al. [17]. Binding gels were composed of Oasis<sup>®</sup> HLB binding phase (7% m/V) embedded in agarose gel (1.5% m/V) whereas diffusive gels were composed of agarose only. The thickness of the diffusive and the binding gel was 0.75 and 0.50 mm respectively. A polyether sulfone (PES) protective membrane with a 0.15 mm thickness was used. As suggested by Guibal et al. [18], the PES membranes were washed with MeOH/UPW before use to avoid the release of polyethylene glycol.

The o-DGT and Lo-DGT devices had exactly the same configuration except their holder, inducing a 4.8-fold increased sampling area (15.2 cm<sup>2</sup> versus 3.14 cm<sup>2</sup>). The o-DGT were prepared using standard DGT holders whereas the Lo-DGT were prepared using Chemcatcher holders (**Figure 1** and picture in **Figure S1**). Thus, only the diameter of the gels differed between the two types of DGT (45 mm for Lo-DGT versus 24 mm for o-DGT).

After exposure, the DGT devices were dismantled, and the binding gels were recovered for elution. In case of low accumulated masses, an evaporation step of the eluates was performed before analysis to lower the limits of quantification.



**Figure 1: o-DGT and Lo-DGT configuration.**

### 2.3 DGT concentration determination

The solution concentration estimated by o-DGT and Lo-DGT,  $C_w$ , was calculated using **Equation 1** [13]:

$$C_w = \frac{m\Delta g}{DA t} \quad \text{Equation 1}$$

where  $m$  is the accumulated mass of the compound in the sampler,  $\Delta g$  is the thickness of the diffusive layer (0.090 cm considering the thickness of the diffusive gel plus the filter membrane),  $D$  is the diffusion coefficient of the compound in the diffusive gel,  $A$  is the sampling area (3.14 cm<sup>2</sup> and 15.2 cm<sup>2</sup> for o-DGT and Lo-DGT respectively), and  $t$  is the deployment time.  $D$  values were corrected for temperature ( $T$ ) using the Stokes-Einstein equation (**Equation 2**) where  $\eta$  is the water viscosity (taken from NIST chemistry WebBook [19]):

$$\frac{D_1 \times \eta_1}{T_1} = \frac{D_2 \times \eta_2}{T_2} \quad \text{Equation 2}$$

### 2.4 Calibration parameters

#### 2.4.1 Diffusion coefficients

The diffusion coefficients of the 24 studied pesticides and metabolites in agarose diffusive gel were determined in triplicate at  $20 \pm 1^\circ\text{C}$  by the method of the diffusion cell described by Zhang and Davison [20]. The diffusion was studied from a source compartment containing  $1 \text{ mg L}^{-1}$  of each pesticide to a pesticide-free receptor compartment, both containing a  $10^{-2} \text{ mol L}^{-1}$   $\text{NaNO}_3$  solution ( $\text{pH} = 5.6 \pm 0.2$ ) to set the ionic strength. Samples were taken from both compartments every 30 min during 4 h to determine the mass of compounds that diffused to the receptor compartment over time. The diffusion coefficients ( $D$ ) were calculated according to **Equation 3**:

$$D = \frac{q_m \Delta g}{C_s A} \quad \text{Equation 3}$$

where  $q_m$  is the pesticide flux between the two compartments (estimated from the slope of the linear regression of the diffused mass over time),  $\Delta g$  the diffusive gel thickness (0.75 mm),  $C_s$  the pesticide concentration in the source compartment (mean value over the deployment time) and  $A$  the sampling area (1.77 cm<sup>2</sup>).

### 2.4.2 Binding gels elution

The o-DGT binding gels were eluted according to Challis et al. [17] using 3 x 3 mL of MeOH with sonication (210 W for 2 minutes) after each addition. After pooling, the eluate was filtered through a polytetrafluoroethylene (PTFE) filter. The protocol for the Lo-DGT binding gels was adapted by increasing the volume of methanol to 5 mL for each addition to allow a correct immersion of the larger binding gel. To determine the optimal number of MeOH additions (minimum number leading to the maximal elution factor), five consecutive additions were individually collected and analyzed instead of being pooled.

The elution factors of o-DGT and Lo-DGT were determined by elution of pre-loaded binding gels. The binding gel pre-loading was performed by individual immersion for 16 h in a solution containing  $20 \mu\text{g L}^{-1}$  of each compound. Five replicates were pre-loaded with  $0.2 \mu\text{g}$  and  $1 \mu\text{g}$  of each pesticide for o-DGT and Lo-DGT respectively, to obtain a similar pesticide density ( $64$  and  $65 \text{ ng cm}^{-2}$  respectively). Samples of each exposure solution were taken before and after immersion to determine the accumulated mass of compounds in each binding gel. For each compound, the elution factor was calculated as the mean of the ratios between the eluted mass and the accumulated mass.

In the case of deployments at very low concentrations ( $\text{ng L}^{-1}$  level), the eluates need to be evaporated before analysis due to a sensitivity issue. A recovery factor was thus also determined to correct any loss of compounds during the whole procedure, including both elution and evaporation steps. For this purpose, the same approach with pre-loaded binding gels was applied but with an evaporation step before analysis. This evaporation step consisted in an evaporation to dryness under nitrogen flow followed by a redissolution with  $1.5 \text{ mL}$  of a UPW/MeOH mixture (90:10 V/V). The recovery factor was calculated as the ratio between the recovered mass after evaporation and the initial accumulated mass.

### 2.5 Time-series accumulation

To study the accumulation behavior of o-DGT and Lo-DGT over time, 18 devices of each configuration were exposed in  $30 \text{ L}$  of a continuously stirred  $10^{-2} \text{ mol L}^{-1} \text{ NaNO}_3$  solution spiked with  $30 \mu\text{g L}^{-1}$  of each pesticide and metabolite. The Lo-DGT and o-DGT were exposed in triplicate for 4 h, 8 h, 12 h, 16 h, 20 h and 24 h, then dismantled for elution. The eluates were directly analyzed to determine the accumulated mass.

### 2.6 Field deployment

To highlight the expected higher sensitivity of the Lo-DGT compared to the o-DGT, a field deployment has been performed in two French headwaters (River A and B) identified as having low concentrations of pesticides (total neutral pesticides  $< 0.1 \mu\text{g L}^{-1}$ ) mainly resulting from cultivation of maize and cereals (*c.a.*, 15% of agricultural lands used for agriculture) [10]. The physicochemical characteristics of the waters are presented in **Table S3**. The flow velocity water was well above  $2 \text{ cm s}^{-1}$ , avoiding any issue linked to the presence of a significant DBL [21]. Four Lo-DGT and four o-DGT were simultaneously deployed in each river for 14 days in June 2021. After elution of the binding gels, a preconcentration of the eluates was performed by evaporation. The eluates,  $9 \text{ mL}$  for the o-DGT and  $15 \text{ mL}$  for the Lo-DGT, were evaporated as described in Section 2.4.2, allowing a 6 and 10-fold concentration factors respectively.

### 2.7 Analysis

The 24 pesticides and metabolites were determined by ultra-high performance liquid chromatography (UHPLC 1290 Infinity Agilent, California, USA) coupled to a quadrupole time-of-flight (Q-TOF, 6540 Agilent) as described by Guibal et al. [22]. Briefly, a Zorbax Eclipse Plus C18 Rapid Resolution High-Definition column ( $2.1 \text{ mm} \times 50 \text{ mm}$ ,  $1.8 \mu\text{m}$ ) was used with a gradient of UPW and MeOH with  $5 \text{ mmol L}^{-1}$  of ammonium and 0.1% (V/V) formic acid as eluent. The Q-TOF was equipped with an electrospray ionization source operating in the positive ionization mode. Daily calibration

solutions were prepared at 1, 2, 5, 10, 25, 50 and 100  $\mu\text{g L}^{-1}$ . Six internal standards were added at 100  $\mu\text{g L}^{-1}$  in each standard solution and sample. The instrumental limits of quantification ( $\text{LOQ}_{\text{instrumental}}$ ), representing the lowest concentration in the injected solution required to generate a quantifiable signal ( $\text{RSD} < 30\%$ ) [23], were estimated between 0.1 and 0.5  $\mu\text{g L}^{-1}$ . More details on the analysis conditions are presented in **Table S4**.

## 2.8 Quality assurance

### 2.8.1 Analysis control

During all pesticide analysis by UHPLC-Q-TOF, a blank (UPW) and a control solution (25 or 50  $\mu\text{g L}^{-1}$ , prepared daily) were analyzed every 15 injections.

### 2.8.2 Deployment solutions monitoring

All laboratory experiments were performed at  $20 \pm 1^\circ\text{C}$  in a temperature-controlled room. For each exposure solution, the ionic strength was fixed with  $10^{-2} \text{ mol L}^{-1} \text{ NaNO}_3$ . During DGT exposition, the pH was monitored and remained stable over time ( $5.6 \pm 0.2$ ). The water temperature was measured by a Tinytag temperature logger every 10 min to determine the average temperature used for the diffusion coefficient correction. To control the stability of pesticides concentrations in solution over time, sampling was performed every hour or at each deployment and removal of DGT devices.

For the deployment in river, the temperature of the water was recorded every 10 min by a Tinytag temperature logger, and the physicochemical parameters (detailed in **Table S3**) were measured at the deployment and removal of the DGT devices.

### 2.8.3 o-DGT and Lo-DGT blanks

The absence of contamination during the DGT laboratory study and the field deployment was verified by performing o-DGT and Lo-DGT blanks. During the time-series accumulation in laboratory, three devices of each type were stored at  $4^\circ\text{C}$  during the whole deployment duration and dismantled in a random position with the exposed o-DGT and Lo-DGT. During the field deployment, one DGT of each type was taken on the field and exposed to the air but not deployed in the river. They were then brought back to the laboratory and stored at  $4^\circ\text{C}$  for the rest of the field exposure period (14 days). They were dismantled with the exposed DGT devices in a random position.

### 2.8.4 Sorption onto materials

The absence of pesticides sorption on the Lo-DGT holder was verified by individually soaking three holders in a stirred solution containing 20  $\mu\text{g L}^{-1}$  of each studied pesticide for 16h. In addition, the absence of pesticides sorption or release by the PTFE syringe filters was investigated by filtering a methanol solution with or without pesticides at 20  $\mu\text{g L}^{-1}$ . More details of these studies are presented in the **Supplementary Material (Figure S2)**.

### 2.8.5 Statistical tests

The statistical tests were based on the assumption that the data were normally distributed. Student tests were performed to compare the elution and recovery factors obtained for the two types of DGT and to compare the accumulation of pesticides by o-DGT and Lo-DGT during lab and field deployments. Significant differences were defined as  $p < 0.01$ .

For every graph, uncertainty bars represent the standard deviation of the mean.

## 3 Results and discussion

### 3.1 Diffusion coefficients

The diffusion coefficients of the studied pesticides and metabolites in agarose diffusive gel were determined by the diffusion cell method. For each compound, the evolution of the mass that diffused

in the receptive compartment over time can be fitted using a linear regression (**Figure S3**). The diffusion coefficient values, indicated in **Table 1**, ranged from 4.0 to 5.5 x 10<sup>-6</sup> cm<sup>2</sup> s<sup>-1</sup> with relative standard deviations (RSD) lower than 8% except for Ethidimuron (11%) and Flurochloridone (15%). They were in the same order of magnitude than the diffusion coefficients available in literature [14,17,24] considering the given uncertainties, regardless of the method used (diffusion cell or slice stacking).

**Table 1: Diffusion coefficients (x 10<sup>-6</sup> cm<sup>2</sup> s<sup>-1</sup> at 20°C) in agarose diffusive gel determined in this study by the diffusion cell method (n = 3) compared to the literature data.**

	This study	Literature data
Atrazine	4.49 ± 0.25	3.53 ± 0.14 [17]; 4.0 ± 0.8 [14]; 5.41 ± 0.28 [24]
Carbendazim	5.05 ± 0.18	5.82 ± 0.27 [24]
Chlortoluron	4.80 ± 0.23	-
Cybutryne	4.38 ± 0.29	-
DEA	5.10 ± 0.30	4.0 ± 0.8 [14]
DIA	5.45 ± 0.40	-
Dimethachlor	4.72 ± 0.25	6.4 ± 1.2 [24]
Dimethenamid	4.62 ± 0.31	-
Dimethoate	5.35 ± 0.21	5.83 ± 0.22 [24]
Diuron	4.78 ± 0.21	4.97 ± 0.34 [24]
Epoxiconazole	4.62 ± 0.21	-
Ethidimuron	4.53 ± 0.48	-
Flurochloridone	4.31 ± 0.63	-
Flurtamone	4.10 ± 0.20	-
Hexazinone	4.35 ± 0.23	-
Imidacloprid	4.94 ± 0.25	4.35 ± 0.48 [17]
Isoproturon	4.74 ± 0.18	5.03 ± 0.23 [24]
Metazachlor	4.58 ± 0.20	4.0 ± 0.8 [14]; 6.12 ± 0.61 [24]
S-Metolachlor	4.65 ± 0.26	4.0 ± 0.8 [14]; 4.82 ± 0.31 [24]
Propiconazole	4.51 ± 0.30	5.22 ± 0.21 [24]
Simazine	4.79 ± 0.21	5.0 ± 0.8 [14]; 5.3 ± 1.6 [24]
Tebuconazole	4.38 ± 0.24	3.56 ± 0.71 [24]
Terbutylazine	4.54 ± 0.20	5.01 ± 0.13 [24]
Terbutylazine-2-hydroxy	3.99 ± 0.18	-

[17,24]: Determination by the diffusion cell method

[14]: Determination by the slice stacking method

## 3.2 Elution procedure

### 3.2.1 Optimization of the Lo-DGT binding gels elution

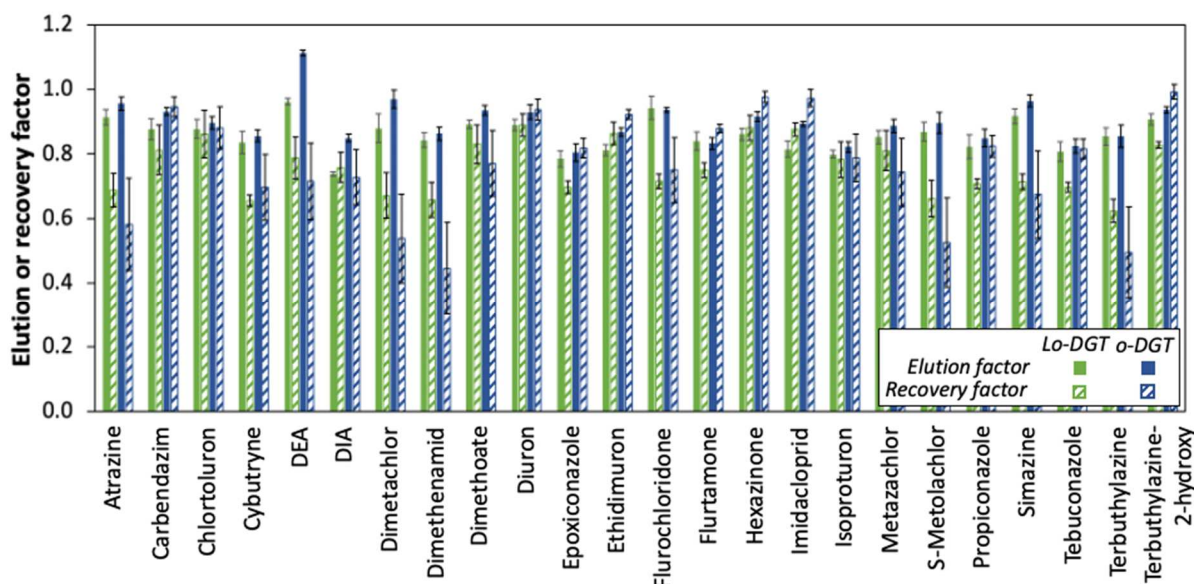
The higher area of the Lo-DGT binding gel requires the addition of a higher volume of MeOH, at least to allow a full immersion. It has been found that 5 mL of MeOH were sufficient for a total immersion of the binding gel. This 1.7-times increase of volume is however lower than the 4.8-times increase of the area. The liquid/solid ratio for the elution of the Lo-DGT binding gels is consequently lowered, which can lead to a potential partial solvent saturation, resulting in lower elution factors. Consequently, five successive additions of 5 mL of MeOH were performed, and the eluted mass was determined for each individual addition. The **Figure S4** shows the cumulative elution factors of Carbendazim as an example, all compounds displaying a similar trend.

An increase of the cumulative elution factor was observed for all the studied compounds from one addition (average elution factor of the 24 compounds: 0.63 ± 0.05) to three (0.91 ± 0.06 on average). In contrast, the two last additions did not improve the elution factor (0.93 ± 0.06 on average). Consequently, the optimal elution conditions for the Lo-DGT binding gels were set to three consecutive additions of 5 mL of MeOH with 210 W sonication for 2 minutes that were recovered and pooled.

### 3.2.2 Elution factors

The elution factors were determined for each of the 24 studied compounds by applying the optimized elution procedure for the Lo-DGT and the conventional elution procedure for o-DGT. The corresponding results are presented in **Figure 2** (detailed in **Table S5**). Depending on the compound, the elution factor ranged from 0.74 to 0.96 and from 0.80 to 1.11 for Lo-DGT and o-DGT respectively, with a high repeatability (RSD < 5%) for both devices. No significant difference ( $p < 0.01$ ,  $n = 3$  to 5) was observed between the elution from o-DGT and Lo-DGT, except for six compounds (DEA, DIA, Dimethoate, Ethidimuron, Hexazinone and Imidacloprid) for which the elution factors were 5% to 15% lower for the Lo-DGT. For DEA, an elution factor higher than 1 was obtained for the o-DGT. Considering the analytical uncertainties, this value (1.11) cannot be considered as effectively higher than 1. As a result, the elution factor was set to 1.0 for this compound.

These results reveal that the elution procedure applied for the o-DGT can be effectively transposed to the Lo-DGT by only increasing the volume of MeOH for a total gel immersion (*i.e.*, 5 mL). Despite the lower MeOH to gel volume ratio, the elution procedure optimized for the Lo-DGT offers the same efficiency than the conventional o-DGT elution for most of the studied compounds, without increasing the number of extraction cycles.



**Figure 2: Elution factors and recovery factors including the evaporation step obtained by Lo-DGT and o-DGT ( $n = 3$  to 5).**

### 3.2.3 Impact of evaporation

In case of low accumulated masses, an evaporation step is needed to perform a preconcentration of the eluates before analysis. However, this step can induce losses of analytes, leading to reduced recovery factors. Except for ten compounds (Carbendazim, Chlortoluron, DEA, DIA, Diuron, Ethidimuron, Hexazinone, Imidacloprid, Isoproturon and Metazachlor), the recovery factors including the evaporation step were significantly lower ( $p > 0.01$ ,  $n = 3$  to 5) than the elution factors (ranging between 0.62 and 0.89 for the Lo-DGT and between 0.44 and 0.99 for the o-DGT) (**Figure 2**), independently of the design of the sampler.

Despite the lower recoveries (up to 27% and 49% decrease for the Lo-DGT and the o-DGT respectively), the evaporation step still offers an analytical benefit considering that 6 or 10-fold concentration factors are obtained. However, in most cases, the addition of the evaporation step also induced a lower repeatability, with RSD increasing up to 11% and 32% for the Lo-DGT and the o-DGT respectively (compared to < 5% without the evaporation step). As a result, it appears preferable to perform the evaporation step only when the accumulated mass is supposed to be too low to be directly

quantified (*i.e.*, in the sub 10 ng range). In this study, the evaporation step was therefore only performed for the field study.

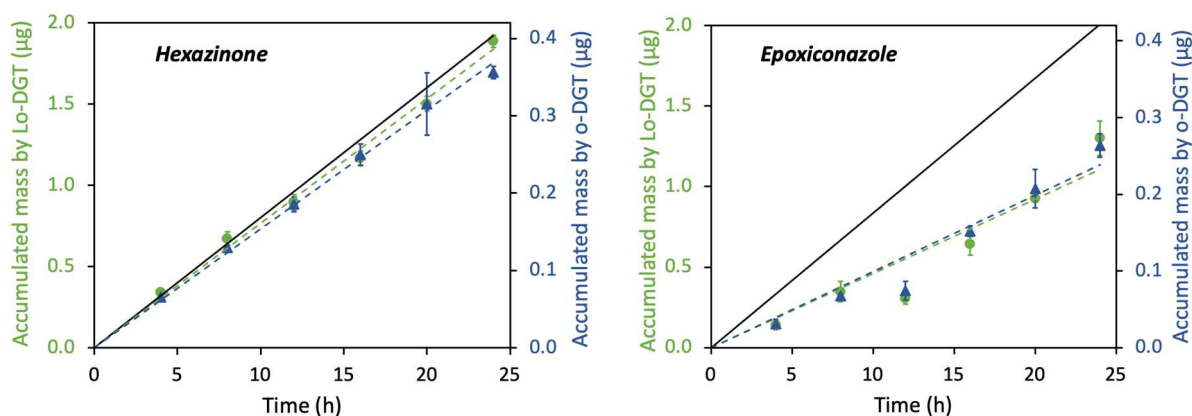
### 3.3 Time-series accumulation

To check the applicability of the DGT theory to the Lo-DGT, a time-series accumulation was performed in identical lab-controlled conditions for both o-DGT and Lo-DGT. According to the DGT quantification model (**Equation 1**), when deployed in a solution with a constant concentration, a linear mass accumulation must be observed over time (providing steady state establishment fulfilled and being below saturating conditions for the binding gel). In the absence of pesticides contamination in the DGT devices, the linear regression of the accumulated mass according to time should have a zero-intercept. Furthermore, the accumulation being expected to be proportional to the sampling area, a 4.8-fold higher accumulation should be obtained for the Lo-DGT compared to the o-DGT.

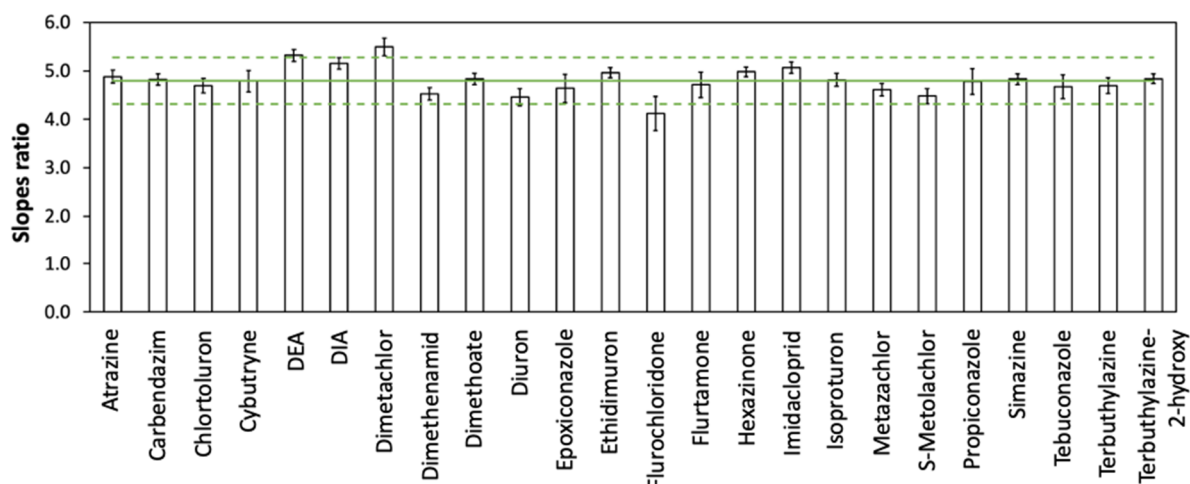
The monitoring of the exposure solution shown that the concentrations were stable over the 24 h deployment (variation lower than 8%). Moreover, the study of the DGT blanks revealed an absence of contamination. Therefore, the accumulation profile of each compound should behave linearly and with a zero-intercept as explained above. A predicted accumulation profile over time was calculated for the o-DGT and the Lo-DGT according to **Equation 1**, based on the average concentration of each pesticide or metabolite and the diffusion coefficients values determined in this study.

#### 3.3.1 Accumulation profiles

Typical examples of the experimental accumulation profiles obtained by Lo-DGT and o-DGT are provided in **Figure 3** (profiles for all compounds are given in **Figure S5**). The accumulation by o-DGT and Lo-DGT appeared linear for most pesticides and metabolites with a zero-intercept, which is consistent with the DGT theory. For every tested compound, no difference was observed between the accumulation profiles of the o-DGT and the Lo-DGT. The accumulation slopes, representing the accumulation flux within the sampler, were determined for each device and each compound, and compared for both designs using the ratio Lo-DGT to o-DGT slope values (**Figure 4**). A constant value of  $4.8 \pm 0.3$  was obtained, which was expected based on the increase of the sampling area (predicted value from **Equation 1**). Consequently, for the 24 studied compounds, the Lo-DGT leads to a higher accumulation flux that is strictly proportional to the increase of sampling area. These results show that, in the tested conditions, the Lo-DGT behavior can be perfectly predicted by the model used for conventional o-DGT. This indicates that enlarging the device by a factor of 4.8 did not significantly change the lateral diffusion contribution or, at least, that the hypothesis of a compensation between the impacts of the lateral diffusion and the DBL is still valid for the Lo-DGT. As a result, when applying the DGT model to quantify the time-averaged concentration, both designs are expected to give the same results.



**Figure 3: Typical examples of time-series accumulation by Lo-DGT (green circles) and o-DGT (blue triangles). The dotted lines represent the experimental linear accumulation by DGT ( $n = 3$ ), and the solid line represents the predicted accumulation. For each graph, the y-axis differ by a factor of 4.8.**

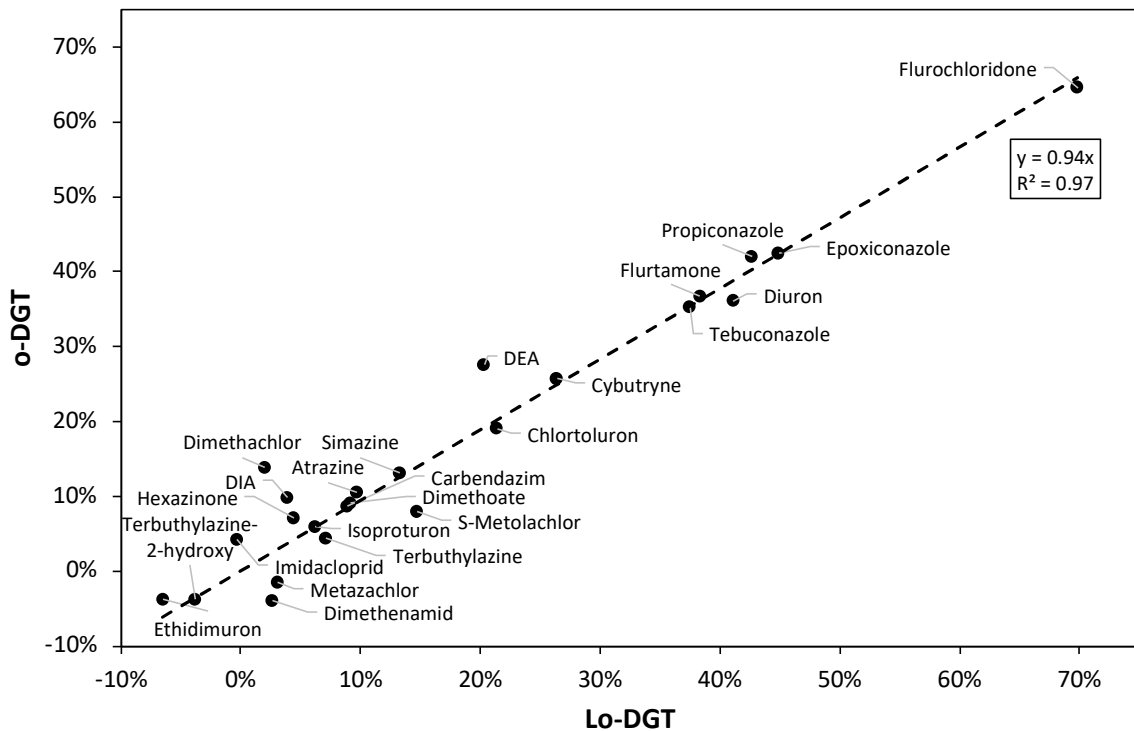


**Figure 4: Ratio of accumulation regression slopes of Lo-DGT to o-DGT. The green lines represent the expected 4.8-ratio with 10% uncertainty.**

### 3.3.2 Comparison with the predicted accumulation

To check the accuracy of the DGT quantification model, the experimental profiles were compared to the predicted one. Two groups of compounds could be distinguished. For the first one, including 15 pesticides and metabolites (Atrazine, DIA, Carbendazim, Dimethachlor, Dimethenamid, Dimethoate, Ethidimuron, Hexazinone, Imidacloprid, Isoproturon, Metazachlor, S-Metolachlor, Simazine, Terbutylazine and Terbutylazine-2-hydroxy) and illustrated by Hexazinone in **Figure 3**, the experimental accumulation by o-DGT and Lo-DGT was consistent with the prediction. Indeed, the experimental and predicted slopes fit with less than 15% deviation (other compounds are given in **Figure S5**). This small deviation can probably result mainly from the analytical uncertainties during the determination of the accumulated masses. The second group, consisting in nine compounds (Chlortoluron, Cybutryne, DEA, Diuron, Epoxiconazole, Flurochloridone, Flurtamone, Propiconazole, Tebuconazole) and illustrated by Epoxiconazole in **Figure 3**, shows deviations from 20% to 70% with the predicted slopes (other compounds are given in **Figure S5**). These deviations could be attributed to bias in the determination of the diffusion coefficients by the diffusion cell method, which does not take into consideration some phenomena such as interactions with the membrane. Indeed, Wang et al [25] have already shown that sorption onto the membrane can induce an accumulation deviation from the prediction during the early deployment times. The hydrophobic compounds were found particularly concerned by adsorption on the PES membranes [2]. However, in our case, the hydrophobicity of the studied compounds cannot fully explain the observed deviation on its own since several compounds with  $\log K_{ow}$  of the same order of magnitude shown deviations ranging from less than 10% to 70% with the prediction (**Figure S6**). Therefore, the exact cause of this phenomenon still needs to be elucidated. However, whereas its origin is not clear, in most cases the deviation seems similar for the o-DGT and the Lo-DGT, meaning that the phenomenon is not affected by the design of the sampler. To highlight this point, a linear regression of the deviation from the predicted accumulation observed with the o-DGT as a function of the deviation observed with the Lo-DGT is presented in **Figure 5**. The resulting slope has a value close to 1 and consistent for all compounds ( $0.94 \pm 0.04$ ), which confirms that this phenomenon is mostly compound-dependent but not device-dependent.

At this stage, it can thus be concluded that the enlarged o-DGT design has the same working behavior and appears to respect the same principles than the conventional o-DGT.



**Figure 5: Slope deviation between experimental and predicted profiles during o-DGT and Lo-DGT time-series accumulation.**

### 3.3.3 Comparison to other enlarged DGT-based samplers

In order to discuss the impact of increasing the sampling area on DGT behavior, results from this study were compared to those existing in the literature for larger configurations of DGT-based samplers [14,15]. The comparison is performed through the sampling ability of each sampler using its sampling rate ( $R_s$ ).  $R_s$  values for Lo-DGT and o-DGT from this study and for the sampler developed by Belles et al. [14] were determined using Equation 4 [17]. For comparison purpose, all values were corrected to the same temperature (20°C) and diffusive layer thickness (1.0 mm).  $R_s$  values were already provided by Urik and Vrana [15] for these temperature and thickness.

$$R_s = \frac{DA}{\Delta g} \quad \text{Equation 4}$$

Regardless of the design, the mean  $R_s$  values clearly show a trend according to the exposure area of the sampler (**Figure S7**). When considering the two samplers investigated in this study (identical configuration and targeted compounds) and the data from Belles et al. [14] restricted to the five common compounds (Atrazine, DEA, Metazachlor, Metolachlor and Simazine), a strong linear relationship is observed. Therefore, the slight discrepancy observed for the data from Urik and Vrana [15] might be mainly a consequence of the discrepancy in the studied compounds. Furthermore, the presence of a nylon net in the diffusive gel might also disturbed the diffusion of the compounds and thus their sampling rate. Overall, the trend followed by all the samplers indicates that their sampling ability is mostly linked to their exposure area. Therefore, using any of these samplers, the basic DGT equation (**Equation 1**) might give an accurate estimation of the TWAC. The larger design from Belles et al. [14] will offer higher sampling rates and therefore higher sensitivity. However, this design is currently not commercially available.

### 3.4 Analytical performances and field validation

#### 3.4.1 Limits of quantification

The LOQ<sub>Lo-DGT</sub> and LOQ<sub>o-DGT</sub> were determined to estimate the lowest concentration in water ( $C_w$ ) that can be quantified for a conventional deployment of 14 days at 19°C, including an evaporation step of the eluates before analysis. The LOQ determination is commonly based on blanks analysis. In this study, no contamination could be detected neither in o-DGT, nor in Lo-DGT blanks. As a result, the DGT LOQ were directly calculated from the instrumental LOQ, converted into the minimal quantifiable  $C_w$  using **Equation 1**. The resulting values are presented in **Table 2**.

The LOQ<sub>Lo-DGT</sub> ranged from 0.2 to 1.3 ng L<sup>-1</sup> against 0.8 to 8.1 ng L<sup>-1</sup> for the LOQ<sub>o-DGT</sub>. This 5-fold decrease in LOQ is consistent with the 4.8 times higher accumulation observed for the Lo-DGT. The improvement of LOQ is of particular interest considering that pesticides can be present at a few ng L<sup>-1</sup> or less in the rivers, which is below or at the limit of the o-DGT quantifying capacity.

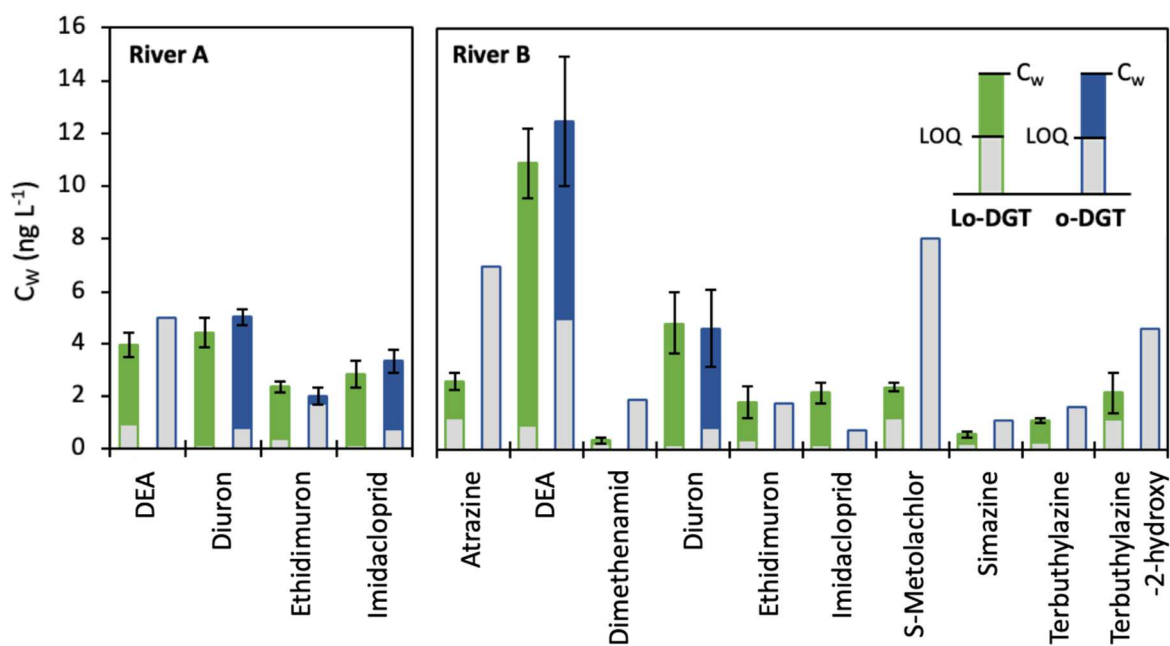
**Table 2: LOQ of pesticides and metabolites for o-DGT and Lo-DGT for a conventional 14-days deployment at 19°C including an evaporation step of the eluates before analysis.**

	LOQ <sub>o-DGT</sub> (ng L <sup>-1</sup> )	LOQ <sub>Lo-DGT</sub> (ng L <sup>-1</sup> )
Atrazine	7.0	1.2
Carbendazim	3.8	0.9
Chlortoluron	0.9	0.2
Cybutryne	6.0	1.3
DEA	5.0	0.9
DIA	4.6	0.9
Dimethachlor	7.2	1.2
Dimethenamid	1.9	0.2
Dimethoate	0.9	0.2
Diuron	0.8	0.2
Epoxiconazole	4.8	1.2
Ethidimuron	1.7	0.4
Flurochloridone	5.7	1.2
Flurtamone	1.0	0.2
Hexazinone	0.9	0.2
Imidacloprid	0.8	0.2
Isoproturon	1.0	0.2
Metazachlor	1.1	0.2
S-Metolachlor	8.1	1.2
Propiconazole	2.0	0.5
Simazine	1.1	0.2
Tebuconazole	5.1	1.2
Terbuthylazine	1.6	0.3
Terbuthylazine-2-hydroxy	4.6	1.1

#### 3.4.2 River deployments

The o-DGT and the Lo-DGT were then compared during a conventional 14-days field deployment in two rivers with low concentrations of pesticides (total neutral pesticides < 0.1 µg L<sup>-1</sup> [10]). In this low-contaminated context, the o-DGT would potentially be not sensitive enough to quantify compounds at the ng L<sup>-1</sup> level whereas the Lo-DGT could be expected to provide a better assessment of the contamination considering its higher sensitivity.

In a first step, the quantification capacity of the two devices were compared. Among the 24 studied pesticides and metabolites, four and ten compounds were quantified by Lo-DGT in rivers A and B respectively, whereas only three and two compounds could be quantified by o-DGT (**Figure 6**). Different situations were observed while comparing the o-DGT and Lo-DGT results. Imidacloprid was quantified in river B with the Lo-DGT at a concentration higher than the  $LOQ_{o-DGT}$  but could not be quantified by the o-DGT, without obvious explanation. In three cases (DEA in river A, Ethidimuron and Terbutylazine in river B), the compounds could only be quantified with the Lo-DGT, their concentrations being slightly below the  $LOQ_{o-DGT}$ . Finally, Atrazine, Dimethenamid, S-Metolachlor, Simazine and Terbutylazine-2-hydroxy were only quantified in river B with the Lo-DGT at concentrations from 2 to 5 times lower than the  $LOQ_{o-DGT}$ . These results highlight that with its increased sampling area, and thus lowered LOQ, the Lo-DGT allows a better assessment of the rivers



**Figure 6: Concentration of pesticides and metabolites ( $C_w$ ) determined by Lo-DGT and o-DGT ( $n = 4$ ) in the rivers A and B compared to the LOQ for a 14-days field deployment.**

contamination by significantly increasing the quantification frequency in a low-contamination context. This is illustrated by Ethidimuron in river A (**Figure 6**) for which the  $C_w$  was 6-times higher than the  $LOQ_{Lo-DGT}$  whereas it was just above the  $LOQ_{o-DGT}$ , ensuring a more reliable value.

In a second step, the  $C_w$  values determined for the compounds quantified by both devices were compared. It should be noted that Diuron and DEA shown accumulation profiles with a significant deviation from the predicted accumulation during the laboratory study. For these two compounds, the  $C_w$  values are thus only an estimation made to allow comparing the two samplers, but they may underestimate the real contaminations. No significant differences could be detected ( $p < 0.01$ ) between the  $C_w$  obtained by o-DGT and Lo-DGT. These results are consistent with the behavior observed during the laboratory deployment with an accumulation that appears strictly proportional to the sampling area.

#### 4 Conclusions

The objective of this study was to verify that increasing the sampling area of the conventional o-DGT allows improving its sensitivity while still respecting the DGT quantification model. Neutral pesticides and metabolites covering a wide range of hydrophobicity ( $\log K_{ow}$  from 0.43 to 3.95) and chemical

groups were studied as model compounds. The new design was based on a commercially available holder to make it readily accessible.

This study highlights that the elution procedure of the o-DGT can be easily transposed to the Lo-DGT by simply increasing the volume of eluent to allow a complete immersion of the larger binding gel.

The lab study confirms that the increased sampling area of the Lo-DGT by a factor of 4.8 does not affect the accumulation behavior. Indeed, the accumulation was linear over time for both designs, the only difference being a 4.8-fold increased accumulated mass, proportional to the increase of the sampling area. This shows that, at the studied scale, the compensation between the DBL and the lateral diffusion appears still valid. The simple DGT quantification model is thus directly transposable to the Lo-DGT without modification. This has been also confirmed during a field deployment that resulted in identical time-weighted average concentration estimations by Lo-DGT and o-DGT. For some compounds however, the mass accumulation behavior deviated from the predicted behavior. This phenomenon being identically observed for both o-DGT and Lo-DGT, it is thus not linked to the design of the DGT tool. It is rather attributed to unwanted interactions between these compounds and the filter membrane, as already highlighted in the literature.

A 5-fold improvement of sensitivity is obtained with the larger design of the o-DGT, allowing a better assessment of very low concentrated pollutants. The benefit of this higher sensitivity has been demonstrated during a conventional 14-days deployment in two low contaminated rivers (total neutral pesticides  $< 0.1 \mu\text{g L}^{-1}$ ) for which the Lo-DGT shown a higher quantification frequency than the o-DGT. Consequently, the Lo-DGT appears more suitable than the o-DGT for pesticides monitoring and deserves further studies regarding its interest for a wider panel of organic compounds. The variety of properties of the studied compounds suggests that these conclusions could be valid for other kinds of micropollutants.

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## o-DGT sensitivity improvement

