Development and validation of an *in situ* high-resolution technique for measuring antibiotics in sediments

Yanying Li[a,b], Qiuyu Rong[c], Chao Han[d], Hanbing Li[e], Jun Luo[b], Liying Yan[b], Degao Wang[a], Kevin C. Jones[b,c,*] and Hao Zhang[c,*]

[a] College of Environmental Science and Engineering, Dalian Maritime University, Dalian, Liaoning 116023, P. R. China

[b] State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing, Jiangsu 210023, P. R. China

[c] Lancaster Environment Centre, Lancaster University, Lancaster, LA1 4YQ, U.K.

[d] Nanjing Institute of Geography & Limnology, Chinese Academy of Sciences, Nanjing, Jiangsu 210008, P. R. China

[e] Department of Environmental Science, Faculty of Environment and Life, Beijing University of Technology, Beijing 100124, China

* corresponding authors

E-mail: h.zhang@lancaster.ac.uk; Tel: +44 1524 593899. (Hao Zhang)

k.c.jones@lancaster.ac.uk; Tel: +44 1524 510230. (Kevin C. Jones)

Abstract

Important biogeochemical processes occur in sediments at fine scales. Sampling techniques capable of yielding information with high resolution are therefore needed to investigate chemical distributions and fluxes and to elucidate key processes affecting chemical fates. In this study, a high-resolution diffusive gradients in thin-films (DGT) technique was systematically developed and tested in a controlled sediment system to measure organic contaminants, antibiotics, for the first time. The DGT probe was used to resolve compound distributions at the mm scale. It also reflected the fluxes from the sediment pore-water and remobilization from the solid phase, providing more dynamic information. Through the fine scale detection, a reduction of re-supply was observed over time, which was concentration and location dependent. Compared to the Rhizon sampling method, antibiotic concentrations obtained by DGT probes were less than the pore-water concentrations, as DGT measures the labile fraction of the compounds. The DGT probe was also tested on an intact sediment core sampled from a lake in China and used to measure the distribution of labile antibiotics with depth in the core at the mm scale.

Key words: antibiotics, sediment profile, high-resolution, fluxes

Highlights:

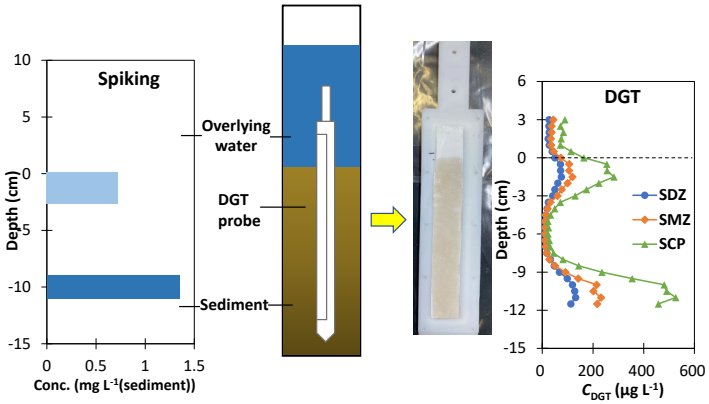
An new *in situ* high resolution sampling probe using DGT technique for studying antibiotics was developed and tested in controlled sediment systems

The resolving power was at the mm scale, better than the Rhizon sampler and conventional slicing.

Vertical distribution of antibiotics in sediments and their transport were determined

The DGT probe was applied to detect antibiotics in an intact sediment core.

Graphical abstract



1. Introduction

Sediments can be both sinks and secondary sources of organic contaminants to the water column. Sorption of compounds onto settling particles can transport them to the bottom sediments, and as compounds become incorporated into sediments and subject to burial, they are removed from the water column [1]. However, if environmental conditions change (e.g. following seasonal redox changes, or physical disturbance of the sediments), sediment bound compounds can be released back into the overlying water [2]. Removal/re-release of chemical compounds at the sediment-water interface and in surface layers of the sediments can be dynamic processes in space and time [3]. Once incorporated into deposited sediments, the vertical concentration profiles can provide information on the input history of contaminants and yield information on the *in situ* degradation of the contaminants [4].

The distribution of contaminants (both vertical and horizontal) in the sediments is often considered to be heterogeneous. Discrete particles, such as phytoplankton and faecal pellets, may act as 'hot spots' in sediments [5]. Physical and chemical properties of sediments – such as redox, pH and organic carbon vary over fine scales, which can affect chemical speciation, microbial activity and decomposition processes [6].

Therefore, to understand mechanistic aspects of the behaviour of contaminants taking place in the sediments, it is necessary to study biogeochemical processes at the appropriate fine scale. This requires a high-resolution sampling technique; given how quickly sediment conditions can change following disturbance or sampling, it is also essential that the high-resolution sampling should be performed *in situ* with minimal disturbance.

Antibiotics are widely used in human therapy, animal husbandry and aquaculture [7]. They are not completely absorbed by the body, with up to 80% of the administered antibiotics excreted as original parent compound or metabolites through feces and urine of patients and livestock into water bodies and soils – then ultimately reaching sediments of aquatic systems [8]. A large fraction of antibiotics used in aquaculture also enter waterbodies and reach sediments directly. Antibiotics in the environment can inhibit the growth of some beneficial microorganisms, change the microbial communities and affect metabolism in ecosystems [9]. Additionally, there is concern about the widespread occurrence of antibiotic residues in the environment, with the potential for development and transfer of resistance, leading to the threat to humans [10]. Antibiotics have been detected in surface waters, ground waters, soils and sediments, up to 100s μg L^{-1} or μg kg^{-1} [11-14]. In sediments, concentrations in the range of 10s – 10000s μg kg^{-1} have been reported around the world [15-17]. There are uncertainties over the persistence, potential for re-mobilisation and re-release, and bioavailability of antibiotics in sediments. Therefore, tools and studies to investigate the distribution and behavior of antibiotics in sediments are needed.

The conventional methods to study the distribution of antibiotics in sediments are centrifugation to remove the pore-water or slicing the sediment core followed by organic solvent extraction of the residues. For example, Li et al. [18] sliced sediment cores at 1 cm intervals, then used the traditional extraction approach. The spatial heterogeneity of contaminants at the micro-scale becomes lost with such methods. These commonly used *ex situ* methods disturb the original sediment environment, including the redox conditions and the equilibrium between solution and solid phase [19]. The Rhizon sampler was developed to collect pore-water from soils by vacuum filtration through a thin porous tube attached to a syringe, although it has not been used for sampling organic chemicals yet. Compared to centrifugation, the Rhizon sampler is a nondestructive *in situ* method which minimizes disturbance of the soil/sediment [20]. However, it can only provide a resolution of 2 – 3 cm, and the small volumes collected (<10 mL) may not be sufficient to detect contaminants present at trace levels. A multi-section peeper was developed to measure the distribution of hydrophobic compounds in sediment porewater, with a resolution of 2 cm [21]. It relied on a laboratory-derived sampling rate (which varied between studies), to estimate the chemical concentrations. DGT (diffusive gradients in thin-films) is an *in situ* high-resolution dynamic technique, which accumulates labile contaminants in pore-waters and their resupply from the solid phase [22]. It provides time weighted average (TWA) concentrations, as a function of deployment time. DGT probes have been used to successfully measure the fluxes and the distribution of metals and nutrients in sediments at high spatial resolutions [23, 24]. This is achieved by diffusion of contaminants followed by uptake into a binding gel,

which can then be sliced to small strips at fine scale (mm) and extracted. By combining the DGT technique with direct computer-imaging densitometry (CID) analysis or laser-ablation (LA) techniques, high resolution of 100s μm have been achieved and new knowledge of biogeochemical processes of inorganics have been obtained [25]. Until now, only 3 studies have used DGT to detect organic contaminants (pesticides, PFASs and antipsychotic drugs) in intact sediment cores [26-28]. However, DGT methods for a wide array of organic compounds – including antibiotics – have been developed and successfully applied in waters and soils [29]. Several studies have been carried out using DGT to measure antibiotics in river waters [30], sea waters [31] and soils [32]. These studies on the application of DGT for *in situ* sampling in sediments and the established DGT methods for antibiotics have laid the foundation for this research.

The aims of this study were therefore: i) to develop, test and validate the use of DGT probes for measuring antibiotics in sediments; ii) to perform laboratory studies on prepared sediments kept under controlled conditions; iii) to test the working conditions for DGT probes and to investigate the mobility of antibiotics spiked into sediment samples and iv) to use the DGT probe on intact lake sediment cores, to test its suitability for sampling the *in situ* distribution of antibiotics.

2. Materials and Methods

2.1 Materials and Preparations

Standard compounds sulfadiazine (SDZ), sulfamethazine (SMZ), sulfachloropyridazine (SCP), clindamycin (CLD, only for field work) and an internal standard sulfamethazine-$^{13}C_6$ (SMZ-$^{13}C_6$) were used for this work (obtained from

131 Sigma-Aldrich). Their selected physico-chemical properties are given in SI Table S1.
132 Stock solutions (1 mg mL^{-1}) of all compounds were made and stored in pure methanol
133 (MeOH). Acetonitrile (ACN) and MeOH of HPLC grade were purchased from Merck
134 (Germany).
135 The configuration of a DGT probe was first described elsewhere [22] and shown in Fig.
136 S1. The probes used here consisted of four layers: a polyethersulfone (PES) filter
137 membrane on the bottom to prevent the binding gel from sticking to the backing plate,
138 a 0.5 mm thick XAD18 binding gel, a 0.8 mm agarose diffusive gel, and a 0.14mm PES
139 filter membrane on the top for protecting the gels. These four layers are held together
140 by an acrylonitrile butadiene styrene (ABS) assembly with an exposure window of 1.8
141 × 15 cm. The probes were purchased from DGT Research Ltd, UK. They were de-
142 oxidized overnight, prior to deployment.

143 **2.2 Laboratory Experiments**

144 The purposes of the lab experiments were to test the performance (method sensitivity,
145 deployment time, reliable spatial resolution) of the DGT probes for sampling antibiotics
146 in sediment cores. To do this, layered sediments (both uncontaminated and spiked) were
147 carefully prepared in a purpose-built tank, which allowed probes to be deployed *in situ*
148 for known times, then removed, and pore-waters to be sampled with minimal
149 disturbance of the sediments.

150 ***Experiment Tank Design***

151 The experiments were conducted in a glass tank designed for DGT probe deployment
152 and pore-water sampling (see Fig. 1(a)). The tank (30 cm (length) × 20 cm (width) ×

30 cm (height)) had 9 pore-water sampling ports (4 mm diameter) on the front. Three upper ports were at -1.5, -5.5 and -9 cm below the sediment surface.

Sediment Preparation

The relatively uncontaminated sediment was collected from the center of Lake Chaohu (Anhui, China) using a gravity corer (Ke Fan, China) [33]. Two different levels of spiking were performed to obtain sediments with 0.46 mg kg^{-1} (low concentration spiking) and 0.85 mg kg^{-1} (high concentration spiking) targeted antibiotics. Each spiked sediment was then well mixed in glass beakers. The high spiking concentrations were used in case the concentrations of target compounds were below detection limits, due to the fast adsorption of the freshly added compounds.

The sediments were transferred to fill the glass tank as shown in Fig. 1(b). The idea was to introduce contaminated and clean layers of sediment into pre-defined positions in the tank and then monitor any dispersal/change of the compound over time, using the probes. This would test the sensitivity and resolution of the probe, and demonstrate the applicability of the probe for detecting spatial and temporal changes of compounds *in situ*. Briefly, a layer of uncontaminated sediment was added to fill the bottom 3 cm of the tank; then a layer (~2 cm) of spiked sediment with high concentration was added; then another 6 cm of uncontaminated sediment was added; then an upper layer (3 cm) of spiked sediment with lower concentration was added. The top of the sediment was then smoothed flat and 6 L freshwater (no target antibiotics detected) was gently added into the tank, avoiding disturbance to the sediment. The depth of water overlying the sediment was ~10 cm. Prior to the experiments, the sediment-water system was then

left to settle for 2 days in a temperature-controlled room at 20.5 °C (the lowest temperature can be achieved in the warehouse) .

The tank was covered with black plastic bags to avoid possible photo-degradation of antibiotics and to minimize artificial stimulation of microbial activity.

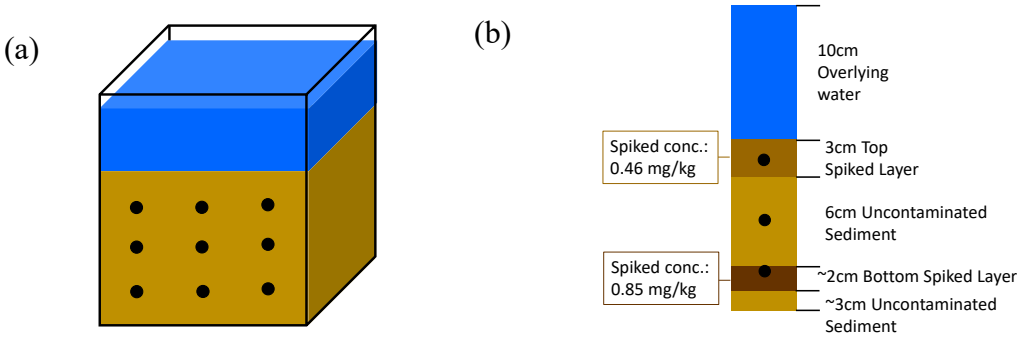


Fig. 1. (a): Sketch of the experiment tank; (b): Distribution of the spiked and uncontaminated sediment introduced into the experimental tank. The black dots are ports for rhizon samplers

DGT Probe Deployment and Pore-water Collection

Test 1: Validation of sampling and analysis performance: A DGT probe (with XAD-18 as binding layer resin, material particle size: 75 – 150 μm) was deployed in a well-stirred solution (0.01M NaCl, pH = 6.0) with known concentrations (given in Fig. 2 and Table S4) of three target compounds for 16 h. The binding gel was sliced into 5 mm strips and analysed following elution procedures described in later section. For the slicing procedures, the gels were cut from the exposure window with a razor blade and the diffusive gel and filter membrane were discarded. The binding gels were sliced to the desired resolutions using a micromanipulator guillotine [34].

Test 2: Investigation of spatial resolution of the technique: Three probes were carefully inserted vertically into the tank. After 24 h, they were retrieved and jet washed with MQ water to remove residual sediment. The binding gels were sliced at 10, 5 and 3 mm

intervals, respectively, to compare the spatial resolutions of the technique.

Test 3: Testing the response of the probes to deployment time: Three probes were inserted into the sediment simultaneously. The deployment was carried out as in Test 2. They were deployed for different time periods (12, 24 and 48 h). The binding gels of the three probes were cut into 5 mm intervals.

Test 4: Comparison of DGT and pore-water sampling: One probe was deployed in sediment tank for 24 hours. Overlying water and pore-water was also sampled (~3 ml per sample) during DGT deployment using 5 cm Rhizon samplers, which were inserted horizontally into the sampling ports at three levels (see Fig. 1).

Test 5: Exploring the behaviour of target compounds in sediments over fine scale: Probes were deployed for 24h at different time series (from Day 1 to Day 15) to visualize the change of distribution and labile concentration of target compounds.

2.3 DGT Application in Intact Lake Sediment Cores

One sediment core (diameter 8 cm, length 60 cm) was collected by gravity corer from the north west of Lake Chaohu, Anhui Province, China with PVC tubes in January 2020 and stored in an incubator (15℃) before deployment of DGT probes. The sampling location was close to the entrance of a river which runs through Hefei city, in an area reported previously to be contaminated with various antibiotics, including 3 target compounds mentioned above [35]. After stabilizing the cores (by keeping them in a 15 ℃ water tank and covered with black plastic bags) in the laboratory for 4 days, DGT probes (XAD 18 – DGT for antibiotics measurement and Chelex-DGT for Fe/Mn redox condition measurement) were deployed for 48 h. The binding gels were sliced at 5 mm

resolutions.

2.4 Sample Treatment and Chemical Analysis

DGT samples: Each gel slice was eluted by 3 mL ACN with 30 min ultrasonic extraction. 0.5 mL of the extractant was sub-sampled and evaporated under a gentle stream of nitrogen to dryness, then reconstituted in a mixed solution of MeOH and MQ water (v/v = 1:9). 0.15 mL of overlying water/pore-water was diluted with MQ water and MeOH to the ratio MeOH: MQ = 1:9.

Lake sediment samples: The two sediment cores collected from the lake were then sliced at 1 cm intervals; each segment was transferred into a 50 mL centrifuge tube and centrifuged at 3000 rpm for 30 min. The pore-water obtained by centrifugation was then pre-concentrated by SPE cartridges (details in the SI). Then ~5 g of the sediment remaining after centrifugation was taken and mixed with 20 mL ACN. The mixture was shaken for 2 h, then centrifuged at 3000 rpm for 20 min. All the extractions and supernatants were evaporated to dryness under a gentle stream of nitrogen and reconstituted in 1 mL with MeOH:MQ = 1:9.

All solutions were filtered through 0.2 μm PTFE syringe filters (Anpel, China) prior to the analysis. The samples were analyzed by UPLC-MS/MS (details in the SI).

2.5 Calculations for DGT Measurements

The principles of using DGT to sample analytes from soils and sediments has been described elsewhere [36]. Briefly, the analytes diffuse through the diffusion layer and are accumulated by the binding gel, leading to a linear concentration gradient in the diffusion layer. As analytes in the pore-water become progressively depleted, the

interfacial concentration (between the DGT probe exposure window and the sediment) of the analytes declines, which induces desorption from the solid phase. DGT therefore accumulates the labile analytes (the fraction that can easily dissociate and resupply) in the sediments and provides a time weighted average (TWA) concentration for the deployment period. Equation (1) was used to calculate the DGT measured concentration (C_{DGT}, μg L^{-1}) at the interface of the sediment and the DGT probe:

$$C_{DGT} = \frac{M \Delta g}{DAt} \quad (1)$$

where, M is the mass of analyte accumulated on the binding gel (ng), t is the deployment time (s), D represents the diffusion coefficient of the analyte in the diffusion layer (cm^2 s^{-1}), A is the sampling area (cm^2, depends on the desired resolution), Δg is the thickness of the diffusion layer (cm). The D values for SDZ, SCP and SMZ at 15℃ (average temperature during the experiment) are 3.73×10^{-6}, 3.32×10^{-6}, and 3.54×10^{-6} cm^2 s^{-1} respectively, according to the previous research [30].

The average flux of analytes (F, ng $cm^{-2}s^{-1}$) from the sediment to the DGT probe during the deployment time (t) and defined sampling area (A), can be obtained using the Equation (2).

$$F = \frac{M}{At} \quad (2)$$

3. Results and Discussions

3.1 Validation of DGT Probe Performance

The quality (accuracy and precision) of the measurements using DGT probes could be influenced by errors introduced from gel cutting, elution procedures and instrumental analysis. Previous studies have shown the homogeneity of the agarose binding gel

incorporated with WAX resin at 3 cm intervals [27], while the measurement of trace metals using DGT probes with a Chelex-100 binding gel had a precision of <10% at a resolution of 1.25 mm [22]. The relative standard deviation of the measurement of three target compounds obtained by the DGT probe with XAD-18 binding gel were all <8% (Fig. 2), and the concentrations derived from DGT were 94 – 102% of the concentrations in the spiked solution. These results confirmed that accurate and precise measurements of antibiotics can be made at high spatial resolution of 5mm using DGT probes.

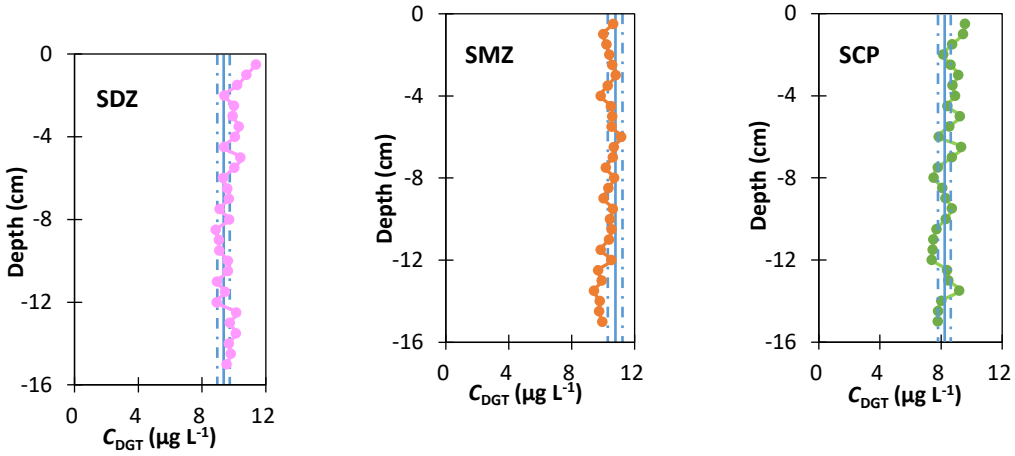


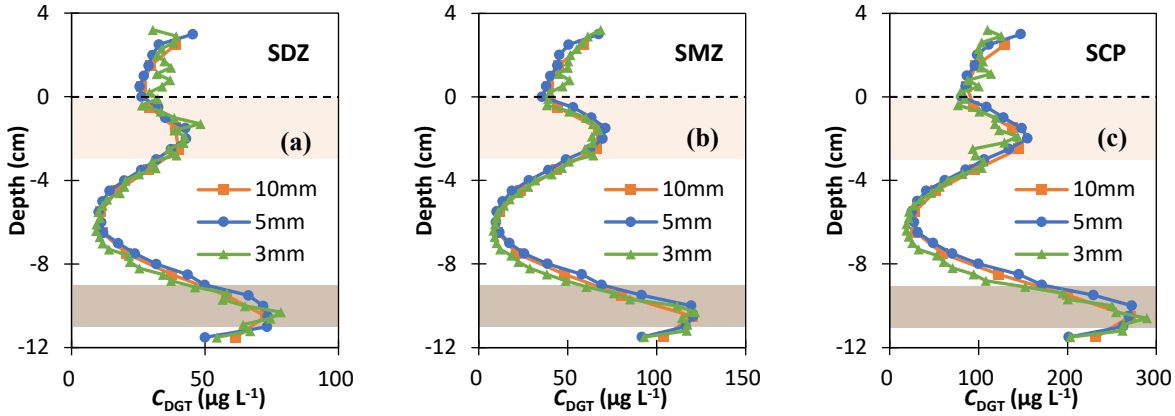
Fig. 2. Concentration profiles of three target antibiotics measured using a DGT probe in a well-stirred solution (deployment time = 16h). Blue solid lines are concentrations of the solution with standard deviations (dotted lines).

3.2 Performance of DGT Probes in Sediments – Laboratory Testing

3.2.1 *Different spatial resolutions*

Observing fine scale heterogeneity of contaminants in sediments relies on achieving appropriate spatial resolution and reliable analysis [37]. As shown in Fig. 3, the 3 vertical concentration profiles obtained with 10, 5 and 3 mm resolutions gave good agreement for the overall concentrations and distributions of each target compound.

277 This suggests i) the sediment tank test system had been prepared with consistent layered
278 structure across the locations where the probes were deployed; ii) DGT probes have the
279 ability to detect accurately the peaks and troughs of antibiotic concentrations at high
280 spatial resolution in the sediment profiles and iii) resolution of 3 mm can be achieved
281 to give more details of the concentration profiles.



282 **Fig. 3.** DGT profiles for 3 target antibiotics at different resolutions (10, 5 and 3 mm).
283 The shaded boxes in the background are the initial spiked layers.

284 **3.2.2** ***Rates of release from the sediment to the DGT probes***

285 DGT samples the labile portion of compound – that in the solution phase, other forms
286 that can pass through the diffusive layer and a desorbed fraction re-supplied from the
287 solid phase when the solution phase is depleted by uptake. Test 2 was designed to
288 investigate the resupply of the antibiotics from the solid phase to DGT probes over time,
289 by comparing the fluxes after 12, 24 and 48 hours of deployment in the tank.

290 This test was conducted at 15 days after the spiking, the peaks of the upper
291 contaminated layers (as shown in Fig. 3) disappeared. As presented in Fig. 4, in the
292 lower concentration areas (~ from sediment surface to -8 cm), the decrease of fluxes
293 from 24 h to 48 h was larger than that from 12 h to 24 h, indicating a gradual reduction

of the resupply of the analytes. In the higher concentration areas (deeper spiked layer from -8 to -11 cm and the overlying water), the opposite situation occurred, showing a fast reduction of re-supply in the beginning, then the rate of re-supply slowed down.

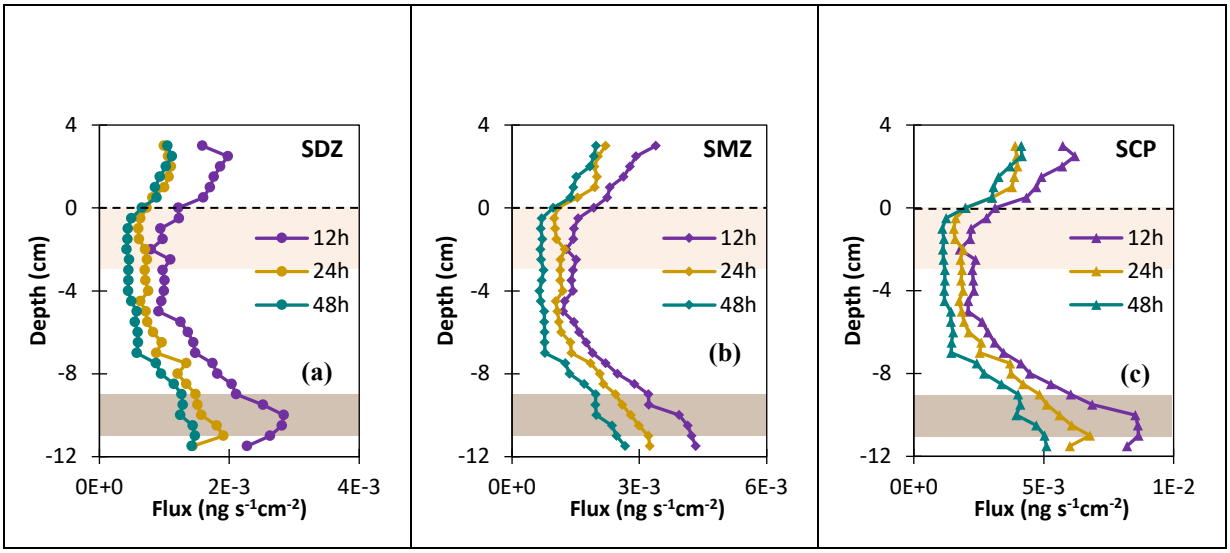


Fig. 4. DGT flux profiles for 3 target antibiotics deployed for different lengths of time (12, 24 and 48 h). The shaded boxes in the background are the original spiked layers.

3.2.3 *Comparison of DGT and Rhizon Pore-water Measurements*

A DGT probe was deployed in parallel with the *in situ* pore-water sampling of the Rhizon samplers. The pore-water sampling could not be undertaken with the same spatial resolution as the DGT sampling (the sampling ports for pore-water were at -1.5, -6 and -9.5 cm, overlying water was sampled at 5 cm), but the profiles of these two approaches were similar. The highest pore-water concentrations occurred at -9.5 cm, the mid-values at -1.5 cm, both in/close to the spiked sediment layers, while the lowest Rhizon sampler concentrations were detected at -5.5 cm in uncontaminated sediment layer (Fig. 5). The concentrations measured at -5.5 cm were low (see Fig. 5), but the detailed data of concentrations measured with the Rhizon sampler at different depths are presented in the Table S5.

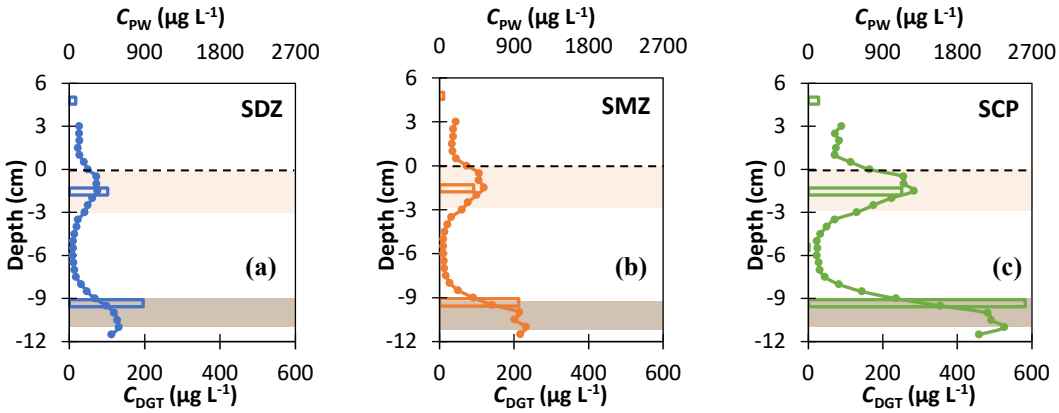


Fig. 5. Concentration-depth profiles of the 3 target antibiotics collected by DGT probe (solid dots) and Rhizon samplers (bar). The shaded boxes in the background are the original spiked layers.

The DGT probe was able to provide the vertical distribution of target analytes in sediments with a much higher resolution. There was good correspondence between the profiles using the two methods in this laboratory-controlled system relied on pre-existing knowledge of the peak locations. In real environments, where the distribution of the analytes is not known in advance, if the spatial resolution of the measurement is not high enough, such peaks may be missed.

Concentrations obtained by Rhizon pore-water sampling (C_{PW}) were 3 – 9 times larger than those of labile antibiotics obtained by DGT sampling (C_{DGT}). This difference has been obtained and explained previously in other studies for other analytes [38, 39]. DGT measures the analytes through an accumulating process, the analytes adjacent to the DGT sampler surface are depleted by DGT accumulation. The re-supply of analytes from that adsorbed on the solid phase is required to sustain the flux from pore-water to the DGT probe. This may be kinetically limited in some cases. DGT only measures labile species that can be desorbed from the sediment and diffused through the

sampler's diffusive gel layer. Some compounds may be complexed and too large to diffuse through the pores of the gel layer. Therefore, it is reasonable to have smaller labile concentrations measured by DGT compared to the total dissolved concentrations by pore-water sampling.

In the overlying water (above 1 cm), the labile concentrations of 3 antibiotics measured by DGT were – on average – 26 (SDZ), 37 (SMZ) and 78 (SCP) μg L^{-1}, again much less than the 78, 51 and 124 μg L^{-1} measured by Rhizon sampling of the water column. Except for the non-labile fraction as explained above, this can mainly be ascribed to the large DBL (diffusive boundary layer) which affects DGT water sampling in the static water-sediment tank [40]. The DBL thickness was measured around 0.44 – 0.45 mm for metals [40] and 0.75 mm on average for some organic contaminants [41] in static solutions. If we take 0.5 mm as the DBL thickness for the target compounds, C_{DGT} values for them were 40 (SDZ), 57 (SMZ) and 119 (SCP) μg L^{-1}, much closer to the measured C_{PW} values.

The R value (C_{DGT}/C_{PW}) has often been used as an indicator of the extent of the depletion of pore-water concentrations at the DGT interface, to reflect the resupply efficiency from the solid phase to pore-water, in response to the depletion by DGT [36]. Higher R values indicate a greater tendency to resupply. If $R \geqslant 0.90$ (indicating that the analytes can be re-supplied rapidly from the solid phase to porewater and then to the DGT probe), this means there is weak binding of the compound to the sediment. If $R <$ 0.1, it normally indicates there is no resupply from the solid phase, supply of the analytes solely depends on the diffusion from the pore-water. If the R value is between

0.1 and 0.9, the analytes in the pore-water are partially sustained, indicating the resupply from the solid phase is slower than the depletion of DGT uptake.

Typical *R* values of the 3 antibiotics in this study at the two different depths are shown in Table 1. The values were different between compounds and varied with sampling depth, being higher in the more reactive upper layer. This is the first time that DGT was used to investigate antibiotics in sediments, so these *R* values are the first set for antibiotics in sediments. Chen et al. [42] measured *R* values of ~0.13 for SMZ in controlled soil experiments, a value close to that in the deeper layer in this study. Here the compounds were freshly added, while in the real environment *R* values might be even lower, as compounds age and become more associated with sediment particles over time [43].

Table 1. R^a values derived for the 3 antibiotics in the controlled sediment study.

Depth (cm)	SDZ	SMZ	SCP
-1.5	0.16	0.29	0.25
-9.5	0.11	0.15	0.14

[a]: $R = C_{DGT}/ C_{PW}$

Time Series Measurements

The concentration profiles of the 3 antibiotics in Fig. 6 and Fig. S2 demonstrate the diffusional transport of these compounds from spiked sediment to the adjacent uncontaminated sediment layers and overlying waters over time. Comparing to Fig. 1(b), the target compounds spread up and down from the 2 discrete layers of contaminated sediments that had been introduced into the tank initially. During the experiment, DGT measured declines in the maximum peak (~ -11 cm) and secondary

peak (~ -1.5 cm), with more rapid decreases from the secondary peak. This may be because compounds in the upper spiked layer dispersed both to the adjacent unspiked layers and overlying waters, while diffusion from the deeper contaminated layer was only through pore-water. According to the Einstein relationship (Eq. 3) [44], the diffusive distance can be roughly estimated.

$$L^2 = 2D_s t_e \quad (3)$$

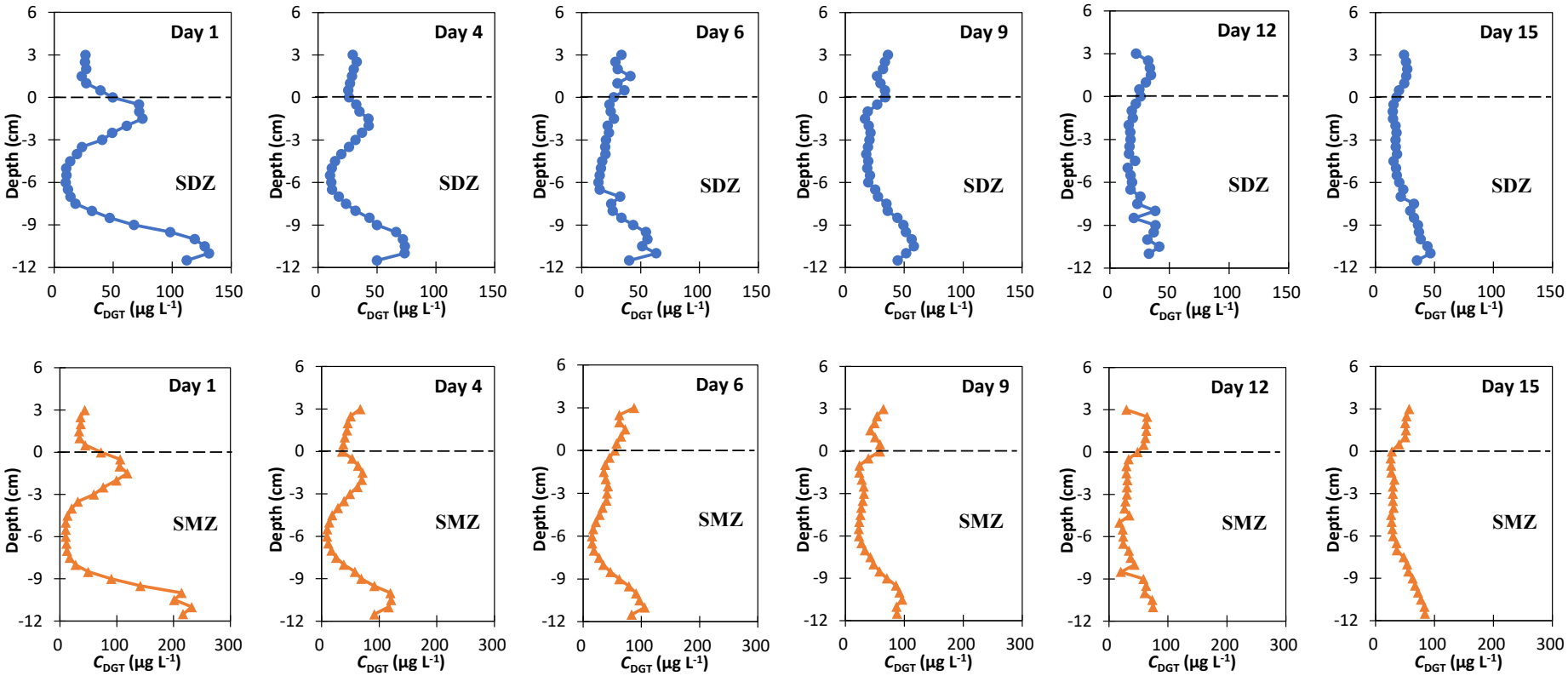
Where L is the diffusive distance (1D), D_s represents the diffusion coefficient in sediments, and t_e is time. The diffusive distances of the 3 target compounds were 0.76 – 0.80 cm after 24 h, while after 15 days, the diffusive distances were 2.94 – 3.11 cm. However, the antibiotics could be detected at greater depths after 24 hours, demonstrating that some transportation of compounds in the sediments had occurred by processes in addition to diffusion. This is evidence that there was some physical disturbance/mixing of some of the original contaminated sediment (probably the finest fraction/colloids) when the system was set up and the tank was settling down. After that (after 24 h) transport is probably mainly controlled by diffusion, with no additional physical mixing/disturbance.

The changes of distribution and concentration of the 3 target compounds in pore-waters showed a similar pattern (see in Fig. S3). In addition to diffusion to and adsorption by adjacent sediments, degradation could also make a little contribution to the changes in concentration. Biodegradation of freshly added SMX has been observed over 24 days after spiking in a non-sterile sediment [45]. Because the tank was covered with black plastic, any photo-degradation should have been minimal.

391 In summary, the changes in the concentrations/profiles of target antibiotics after 24
392 hours of the spiking are believed to be mainly due to adsorption to the sediment particles,
393 since the concentration decrease in the spiked layer was much larger than the increases
394 in unspiked layers during the experiment. Diffusive transfers from the original
395 contaminated layers also contributed to the reduction of compounds from the spiked
396 layers, likely together with a small degree of biodegradation.

397 ***Comparison of Chemical Behaviours***

398 The 3 antibiotics all have high aqueous solubility (77 – 7000 mgL^{-1}) and low/moderate
399 partition coefficients to sediments (log*K*ow from -0.09 to 0.31) [30]. They can therefore
400 readily enter the sediment pore-water and overlying water column. The concentration
401 profiles of these 3 compounds obtained by DGT probes had the same trend as shown in
402 the figures above. Although the spiked concentrations of antibiotics were the same, the
403 labile concentrations measured by DGT probes were in the order of SDZ< SMZ< SCP
404 at all depths (see Fig.5). This order is the opposite to what has been observed in acid
405 soils (pH ranging from 4.5 to 5.1) [46], while the affinity of SCP was less than SMZ in
406 neutral soils [47]. The sediment used in this work was basic with pH of 8.5; this could
407 be the reason for the mobility order of these three antibiotics being opposite to that in
408 acid soils.



409 **Fig. 6**. DGT profiles of SDZ (blue dots) and SMZ (orange triangle) measured at different times
410

411 ***Comments on detection limits and sampling times***

412 Compound-specific detection limits can be derived using eq. 1. In this study, the D
413 values of the target antibiotics were between 3.32×10^{-6} and 3.73×10^{-6} (at 20.5℃), the
414 thickness of the diffusion layer was 0.094 cm, the exposure area (A) was 0.9 cm^2 (for
415 the 5 mm intervals). The IDLs of the target compounds were ~50 ng L^{-1} and final sample
416 volumes (V_0) was typically 1 mL. Therefore, the MQLs (method quantification limit)
417 of DGT sampling were about 16 – 18 ng L^{-1} for deployment of 24 h as in this study.
418 The minimum sampling time for field deployment means the time needed for the
419 amount of target compounds adsorbed by the binding gel to exceed the IDLs. In the
420 present study, taking SDZ as an example, the minimum sampling time (t_{min}) can be
421 calculated by:

422 $$t_{min} = \frac{\Delta g \times M_{IDL}}{D \times A \times C_{DGT}} \quad (3)$$

423 C_{DGT} can be estimated by C_{PW} and an empirical value of R (measured in the range
424 between 0.1 – 0.3 here). M_{IDL} is the mass accumulated on the binding gel (ng), M_{IDL} =
425 IDL × 1000 / V_0. If the IDL was 50 ng L^{-1} (see above), and C_{PW} values in a sediment
426 core are typically 10 – 100 ng L^{-1} [48, 49] then the t_{min} needed will range from 5 hours
427 to 2 days for resolution of 5mm.
428 DGT method sensitivities can be improved (e.g. by a factor of 10), by simply reducing
429 the final sample volumes, increasing the deployment times, reducing the diffusion layer
430 thickness and increasing the exposure areas. The MQLs using the Rhizon sampler were
431 ~16 ng L^{-1} too (assuming the pre-concentration factor = 3). In the real environment, if
432 the concentrations of the target compounds are lower, more pore-water is required to

obtain a higher pre-concentration factor for the Rhizon samplers. Another widely used method to obtain pore-waters samples is slicing the sediment core layers followed by centrifugation. However, this *ex situ* approach would certainly disturb the sediment structures and change the redox conditions and pH, which control chemical speciation and availability. The advantages of the DGT technique are directly sampling *in situ* in field conditions, purer matrix and greater analytical sensitivity.

DGT application in intact lake sediment cores

To validate the application of DGT probes for antibiotics in the real environment, probes were deployed in the top 13 cm of the intact sediment cores collected from the field. In the sediment core collected in Chaohu Lake, only SMZ of the 3 target antibiotics was detectable, concentrations of the other two target compounds were <MDL. The SMZ depth profiles of DGT measured concentrations (C_{DGT}) and pore-water concentrations obtained by slicing and centrifugation (C_{PW}), are shown in Fig. 7 (a and b). Another commonly used antibiotic, clindamycin (CLD) was also detected in the sediment core. The results of concentration profiles of CLD are presented in Fig. 7 (c and d). To assess the redox condition of the sediments, additional information on the DGT measured Fe and Mn profiles is presented in Fig. S4.

The baseline DGT (labile) concentrations of SMZ were quite constant (~ 50 ng L^{-1}) with depth. Two peaks were present at different depths. A slight increase in C_{DGT} was observed around -5.5 cm, while a maximum concentration of 515 ng L^{-1} was observed at -10.5 cm, followed by subsequent decrease below that depth. The C_{PW} profile showed a similar trend to C_{DGT} with two peaks, and the concentration gradually increased to

maximum value of 32.5 ng L^{-1} at -11 cm.

It is an unusual phenomenon that C_{DGT} values at all depths were much higher than C_{PW}. Fe and Mn are oxygen sensitive elements and their concentration profiles can be used to assess the redox condition of the sediment. The concentration profile of labile Fe (II) and Mn (II) measured in the same sediment core is shown in SI Fig. S4, a DGT probe with Chelex-100 in binding layer for trace metals was deployed *in situ* and measured at 5 mm resolution. The results demonstrated that the reduction of Fe and Mn oxides/ hydroxides to labile Fe (II) and Mn (II) occurred in the upper layer of the sediment, intensified at -4.0 cm, below which the sediment was in an anoxic condition. Slicing and centrifugation of the sediment were both conducted in the open air, which destroyed the anoxic condition of the sediment, SMZ may be rapidly adsorbed to the precipitated iron oxides, the degradation of the target compounds might also be accelerated [50]. Therefore, these conventional *ex situ* extraction approaches may seriously underestimate the compound levels detected.

A similar situation was observed for CLD as shown in Fig. 7 (c and d). The profiles of concentrations measured by two methods have comparable shape, with a gradual upward trend above -9.0 cm, then increased sharply at -9 to -10 cm. The C_{DGT} profile has more variations as it was measured at higher resolution. The change of the redox condition also influenced the measurement of CLD concentrations in pore-water, proving that an *in situ* sampling approach, such as DGT, is more suitable for the measurement of compounds in sediments.

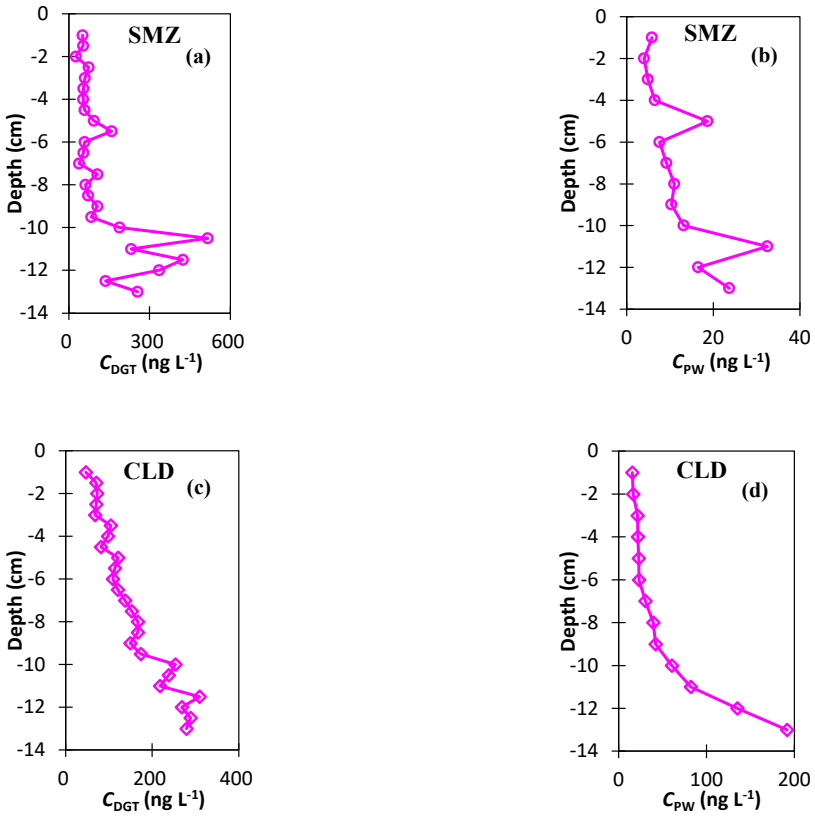


Fig. 7. SMZ and CLD concentration distribution profiles in Lake Chaohu sediments by DGT and pore-water measurements (a: SMZ measured by DGT; b: SMZ measured by pore-water extraction; c: CLD measured by DGT; d: CLD measured by pore-water extraction.

Environmental Implication and Future Research Directions

This is the first systematic study to validate and demonstrate the use of the DGT probe for high spatial resolution (sub-mm/mm scale) sampling of antibiotics in sediments. Deploying probes over 12 – 48 hours, detection limits of 10s ng L^{-1} were readily achieved by this approach and it can be improved by optimizing the deployment conditions. Finer spatial scale measurement can be achieved with suitable detection systems to investigate compound distribution *in situ* at the mm scale. This makes it possible to conduct studies on the influence of redox changes and processes in the surface microlayer of the sediment-water interface, where the exchange, binding and

breakdown of organic compounds can occur. Monitoring *in situ* rates of dissipation, transformation and exchange is now possible.

As a dynamic sampling technique, DGT is able to provide kinetic information in sediments including fluxes, labile pool size and kinetic resupply. In a previous study, kinetic information was determined for pesticides in sediments.[32] In the future, DGT probes can be used together with the DIFS (DGT-induced fluxes in soils and sediments) model, to obtain better knowledge of such processes for antibiotics.

The microcosm study showed that the 3 test antibiotics can rapidly re-mobilise and migrate from sub-surface contaminated layers into clean sediments and overlying water bodies by diffusion transport, adsorption processes and possibly certain degree of biodegradation. In fact, DGT has been developed for several other groups of organic compounds (including personal care products, endocrine disrupting chemicals, pesticides, psychiatric pharmaceuticals and polyfluoroalkyl substances),[51-56] so its application to investigate fine-scale biogeochemical processes in sediments and the sediment-water interface can also be extended to other compound classes. Investigation on the effect of biopertubation and dymanic transport may also possible using DGT technique in different conditions of the sediments.

CRediT authorship contribution statement

Yanying Li: Investigation, Data analysis, Writing – original draft. Qiuyu Rong: Investigation, Validation. Chao Han: Methodology, Sample collection. Hanbing Li: Validation, Methodology. Jun Luo: Supervision, Funding acquisition. Liying Yan: Investigation, Data analysis. Degao Wang: Supervision. Kevin C. Jones:

Conceptualization, Supervision, Writing – review & editing, Funding acquisition. Hao Zhang: Conceptualization, Supervision, Writing – review & editing, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The authors do not have permission to share data.

Acknowledgement

This work was supported by the Fundamental Research Funds for the Central Universities (3132022158), and the National Natural Science Foundation of China (No. 42077360 and 52200223).

Supporting Information

Supplementary data associated with this article can be found in the online version at Additional information as noted in the text including analytical methods, five tables and four figures.

References

[1] Huang, Y., Wang, Y., Huang, Y., Zhang, L., Ye, F., Wang, J., Shang, J., Liao, Q., 2020. Impact of sediment characteristics on adsorption behavior of typical antibiotics in Lake Taihu, China. Science of the Total Environment 718, 137329.

[2] Xia, X., Teng, Y., Zhai, Y., Zheng, F., Cao, X., 2022. Influencing factors and mechanism by which DOM in groundwater releases Fe from sediment. Chemosphere 300, 134524.

[3] Duan, L., Song, J., Yin, M., Yuan, H., Li, X., Zhang, Y., Yin, X., 2021. Dynamics of arsenic and its interaction with Fe and S at the sediment-water interface of the seasonal hypoxic Changjiang Estuary. Science of the Total Environment 769, 145269.

[4] Tham, T.T., Anh, H.Q., Phuong, B.T., Thuy, N.T.T., Yen, N.T.H., Tri, T.M., Minh, T.B., 2020. Contamination status and temporal trends of persistent toxic substances in sediment cores from coastal areas of central Vietnam. Marine Pollution Bulletin 156, 111222.

[5] Piarulli, S., Airoldi, L., 2020. Mussels facilitate the sinking of microplastics to bottom sediments and their subsequent uptake by detritus-feeders. Environmental Pollution 266, 115151.

[6] Guan, D.X., Williams, P.N., Xu, H.C., Li, G., Luo, J., Ma, L.Q., 2016. High-resolution measurement and mapping of tungstate in waters, soils and sediments using the low-disturbance DGT sampling technique. Journal of Hazardous Materials 316, 69-76.

[7] Zhang, J., Zhang, X., Zhou, Y., Han, Q., Wang, X., Song, C., Wang, S., Zhao, S., 2023. Occurrence, distribution and risk assessment of antibiotics at various aquaculture stages in typical aquaculture areas surrounding the Yellow Sea. Journal of Environmental Sciences 126, 621-632.

[8] Bavumiragira, J.P., Yin, H., 2022. Fate and transport of pharmaceuticals in water systems: A processes review. Science of the Total Environment 823, 153635.

[9] Shahen, M.Z., Mahmud, S., Rony, M., Sohana, S., Imran, M., Al Maruf, M., Azim, M., Islam, M., Islam, M., Uddin, M., 2019. Effect of antibiotic susceptibility and inhibitory activity for the control of growth and survival of microorganisms of extracts of Calendula officinalis. European Journal of Medical and Health Sciences 1 (1), 1-9.

[10] Wu, J., Wang, J., Li, Z., Guo, S., Li, K., Xu, P., Ok, Y.S., Jones, D.L., Zou, J., 2022. Antibiotics and antibiotic resistance genes in agricultural soils: A systematic analysis. Critical Reviews in Environmental Science and Technology 53 (7), 1-18.

[11] Zhou, Q., Liu, G., Arif, M., Shi, X., Wang, S., 2022. Occurrence and risk assessment of antibiotics in the surface water of Chaohu Lake and its tributaries in China. Science of the Total Environment 807, 151040.

[12] Li, M., Yang, L., Yen, H., Zhao, F., Wang, X., Zhou, T., Feng, Q., Chen, L., 2023. Occurrence, spatial distribution and ecological risks of antibiotics in soil in urban agglomeration. Journal of Environmental Sciences 125, 678-690.

[13] Tang, J., Wang, S., Fan, J., Long, S., Wang, L., Tang, C., Tam, N.F., Yang, Y., 2019. Predicting distribution coefficients for antibiotics in a river water–sediment using quantitative models based on their spatiotemporal variations. Science of the Total Environment 655, 1301-1310.

[14] Kairigo, P., Ngumba, E., Sundberg, L.-R., Gachanja, A., Tuhkanen, T., 2020. Occurrence of antibiotics and risk of antibiotic resistance evolution in selected Kenyan wastewaters, surface waters and sediments. Science of the Total Environment 720, 137580.
[15] Huang, Y.H., Liu, Y., Du, P.P., Zeng, L.J., Mo, C.H., Li, Y.W., Lü, H., Cai, Q.Y., 2019. Occurrence and distribution of antibiotics and antibiotic resistant genes in water and sediments of urban rivers with black-odor water in Guangzhou, South China. Science of the Total Environment 670, 170-180.
[16] Fernandes, M.J., Paíga, P., Silva, A., Llaguno, C.P., Carvalho, M., Vázquez, F.M., Delerue-Matos, C., 2020. Antibiotics and antidepressants occurrence in surface waters and sediments collected in the north of Portugal. Chemosphere 239, 124729.
[17] Wang, G., Zhou, S., Han, X., Zhang, L., Ding, S., Li, Y., Zhang, D., Zarin, K., 2020. Occurrence, distribution, and source track of antibiotics and antibiotic resistance genes in the main rivers of Chongqing city, southwest China. Journal of Hazardous Materials 389, 122110.
[18] Li, S., Huang, Z., Wang, Y., Liu, Y.-Q., Luo, R., Shang, J.-G., 2018. Migration of two antibiotics during resuspension under simulated wind–wave disturbances in a water–sediment system. Chemosphere 192, 234-243.
[19] Zhang, H., Davison, W., Knight, B., McGrath, S., 1998. In situ measurements of solution concentrations and fluxes of trace metals in soils using DGT. Environmental Science & Technology 32 (5), 704-710.
[20] Steiner, Z., Lazar, B., Erez, J., Turchyn, A.V., 2018. Comparing Rhizon samplers and centrifugation for pore-water separation in studies of the marine carbonate system in sediments. Limnology and oceanography: Methods 16 (12), 828-839.
[21] Liu, H.H., Bao, L.J., Feng, W.H., Xu, S.P., Wu, F.C., Zeng, E.Y., 2013. A multisection passive sampler for measuring sediment porewater profile of dichlorodiphenyltrichloroethane and its metabolites. Analytical Chemistry 85 (15), 7117-7124.
[22] Zhang, H., Davison, W., Miller, S., Tych, W., 1995. In situ high resolution measurements of fluxes of Ni, Cu, Fe, and Mn and concentrations of Zn and Cd in porewaters by DGT. Geochimica et Cosmochimica Acta 59 (20), 4181-4192.
[23] Zhang, H., Davison, W., Mortimer, R.J.G., Krom, M.D., Hayes, P.J., Davies, I.M., 2002. Localised remobilization of metals in a marine sediment. Science of the Total Environment 296 (1-3), 175-187.
[24] Wu, Z., Jiao, L., Wang, S., 2016. The measurement of phosphorus, sulfide and metals in sediment of Dianchi Lake by DGT (diffusive gradients in thin films) probes. Environmental Earth Sciences 75 (3), 1-14.
[25] Guan, D.-X., Williams, P.N., Luo, J., Zheng, J.-L., Xu, H.-C., Cai, C., Ma, L.Q., 2015. Novel precipitated zirconia-based DGT technique for high-resolution imaging of oxyanions in waters and sediments. Environmental Science & Technology 49 (6), 3653-3661.
[26] Li, Y., Han, C., Luo, J., Jones, K.C., Zhang, H., 2021. Use of the Dynamic Technique DGT to Determine the Labile Pool Size and Kinetic Resupply of Pesticides in Soils and Sediments. Environmental Science & Technology 55 (14), 9591-9600.

[27] Yang, Y., Liu, S., Wang, R., Li, C., Tang, J., Chen, T., Ying, G.-G., Chen, C.-E., 2022. Diffusive gradients in thin films (DGT) probe for effectively sampling of per-and polyfluoroalkyl substances in waters and sediments. Journal of Environmental Sciences 121, 90-97.
[28] Ji, X., Challis, J.K., Cantin, J., Perez, A.S.C., Gong, Y., Giesy, J.P., Brinkmann, M., 2022. A novel passive sampling and sequential extraction approach to investigate desorption kinetics of emerging organic contaminants at the sediment− water interface. Water Research 217, 118455.
[29] Guibal, R., Buzier, R., Lissalde, S., Guibaud, G., 2019. Adaptation of diffusive gradients in thin films technique to sample organic pollutants in the environment: An overview of o-DGT passive samplers. Science of the Total Environment 693, 133537.
[30] Chen, C.E., Zhang, H., Ying, G.G., Jones, K.C., 2013. Evidence and recommendations to support the use of a novel passive water sampler to quantify antibiotics in wastewaters. Environmental Science & Technology 47 (23), 13587-13593.
[31] Xie, H., Chen, J., Chen, Q., Chen, C.-E.L., Du, J., Tan, F., Zhou, C., 2018. Development and evaluation of diffusive gradients in thin films technique for measuring antibiotics in seawater. Science of the Total Environment 618, 1605-1612.
[32] Chen, C., Chen, W., Ying, G., Jones, K., Zhang, H., 2015. In situ measurement of solution concentrations and fluxes of sulfonamides and trimethoprim antibiotics in soils using o-DGT. Talanta 132, 902-908.
[33] Han, C., Geng, J.J., Xie, X.C., Wang, X.R., Ren, H.Q., Gao, S.X., 2012. Determination of phosphite in a eutrophic freshwater lake by suppressed conductivity ion chromatography. Environmental Science & Technology 46 (19), 10667-10674.
[34] Shuttleworth, S.M., Davison, W., Hamilton-Taylor, J., 1999. Two-dimensional and fine structure in the concentrations of iron and manganese in sediment pore-waters. Environmental Science & Technology 33 (23), 4169-4175.
[35] Tang, J., Shi, T., Wu, X., Cao, H., Li, X., Hua, R., Tang, F., Yue, Y., 2015. The occurrence and distribution of antibiotics in Lake Chaohu, China: Seasonal variation, potential source and risk assessment. Chemosphere 122, 154-161.
[36] Harper, M., Davison, W., Zhang, H., Tych, W., 1998. Kinetics of metal exchange between solids and solutions in sediments and soils interpreted from DGT measured fluxes. Geochimica et Cosmochimica Acta 62 (16), 2757-2770.
[37] Stockdale, A., Davison, W., Zhang, H., 2009. Micro-scale biogeochemical heterogeneity in sediments: a review of available technology and observed evidence. Earth-Science Reviews 92 (1-2), 81-97.
[38] Ernstberger, H., Zhang, H., Tye, A., Young, S., Davison, W., 2005. Desorption kinetics of Cd, Zn, and Ni measured in soils by DGT. Environmental Science & Technology 39 (6), 1591-1597.
[39] Gao, Y., Leermakers, M., Gabelle, C., Divis, P., Billon, G., Ouddane, B., Fischer, J.-C., Wartel, M., Baeyens, W., 2006. High-resolution profiles of trace metals in the pore waters of riverine sediment assessed by DET and DGT. Science of the Total Environment 362 (1-3), 266-277.
[40] Uher, E., Tusseau-Vuillemin, M.-H., Gourlay-France, C., 2013. DGT measurement in low flow conditions: diffusive boundary layer and lability considerations.

661 Environmental Science: Processes & Impacts 15 (7), 1351-1358.
662 [41] Challis, J.K., Hanson, M.L., Wong, C.S., 2016. Development and calibration of an
663 organic-diffusive gradients in thin films aquatic passive sampler for a diverse suite of
664 polar organic contaminants. Analytical Chemistry 88 (21), 10583-10591.
665 [42] Chen, C., Jones, K., Ying, G., Zhang, H., 2014. Desorption kinetics of sulfonamide
666 and trimethoprim antibiotics in soils assessed with diffusive gradients in thin-films.
667 Environmental Science & Technology 48 (10), 5530-5536.
668 [43] Radke, M., Lauwigi, C., Heinkele, G., Mürdter, T.E., Letzel, M., 2009. Fate of the
669 antibiotic sulfamethoxazole and its two major human metabolites in a water sediment
670 test. Environmental Science & Technology 43 (9), 3135-3141.
671 [44] Harper, M.P., Davison, W., Tych, W., 1997. Temporal, spatial, and resolution
672 constraints for in situ sampling devices using diffusional equilibration: dialysis and
673 DET. Environmental Science & Technology 31 (11), 3110-3119.
674 [45] Zhang, W., Li, Y., Wang, C., Wang, P., Hou, J., Yu, Z., Niu, L., Wang, L., Wang, J.,
675 2016. Modeling the biodegradation of bacterial community assembly linked antibiotics
676 in river sediment using a deterministic–stochastic combined model. Environmental
677 Science & Technology 50 (16), 8788-8798.
678 [46] Conde-Cid, M., Fernández-Calviño, D., Fernández-Sanjurjo, M., Núñez-Delgado,
679 A., Álvarez-Rodríguez, E., Arias-Estévez, M., 2019. Adsorption/desorption and
680 transport of sulfadiazine, sulfachloropyridazine, and sulfamethazine, in acid
681 agricultural soils. Chemosphere 234, 978-986.
682 [47] Conde-Cid, M., Ferreira-Coelho, G., Fernández-Calviño, D., Núñez-Delgado, A.,
683 Fernández-Sanjurjo, M., Arias-Estévez, M., Álvarez-Rodríguez, E., 2020. Single and
684 simultaneous adsorption of three sulfonamides in agricultural soils: Effects of pH and
685 organic matter content. Science of the Total Environment 744, 140872.
686 [48] Xu, J., Zhang, Y., Zhou, C., Guo, C., Wang, D., Du, P., Luo, Y., Wan, J., Meng, W.,
687 2014. Distribution, sources and composition of antibiotics in sediment, overlying water
688 and pore water from Taihu Lake, China. Science of the Total Environment 497, 267-
689 273.
690 [49] Chen, Y., Cui, K., Huang, Q., Guo, Z., Huang, Y., Yu, K., He, Y., 2020.
691 Comprehensive insights into the occurrence, distribution, risk assessment and indicator
692 screening of antibiotics in a large drinking reservoir system. Science of the Total
693 Environment 716, 137060.
694 [50] Pan, M., Chu, L., 2016. Adsorption and degradation of five selected antibiotics in
695 agricultural soil. Science of the Total Environment 545, 48-56.
696 [51] Chen, W., Li, Y., Chen, C., Sweetman, A., Zhang, H., Jones, K., 2017. DGT passive
697 sampling for quantitative in situ measurements of compounds from household and
698 personal care products in waters. Environmental Science & Technology 51 (22), 13274-
699 13281.
700 [52] Chen, W., Pan, S., Cheng, H., Sweetman, A.J., Zhang, H., Jones, K.C., 2018.
701 Diffusive gradients in thin-films (DGT) for in situ sampling of selected endocrine
702 disrupting chemicals (EDCs) in waters. Water Research 137, 211-219.
703 [53] Fang, Z., Li, K., Li, Y., Zhang, H., Jones, K.C., Liu, X., Liu, S., Ma, L.Q., Luo, J.,
704 2019. Development and application of the diffusive gradients in thin-films technique

for measuring psychiatric pharmaceuticals in natural waters. Environmental Science & Technology 53 (19), 11223-11231.
[54] Li, Y., Chen, C.E.L., Chen, W., Chen, J., Cai, X., Jones, K.C., Zhang, H., 2019. Development of a passive sampling technique for measuring pesticides in waters and soils. Journal of Agricultural and Food Chemistry 67 (22), 6397.
[55] Wang, R., Biles, E., Li, Y., Juergens, M.D., Bowes, M.J., Jones, K.C., Zhang, H., 2020. In situ catchment scale sampling of emerging contaminants using diffusive gradients in thin films (DGT) and traditional grab sampling: a case study of the River Thames, UK. Environmental Science & Technology 54 (18), 11155-11164.
[56] Fang, Z., Li, Y., Li, Y., Yang, D., Zhang, H., Jones, K.C., Gu, C., Luo, J., 2021. Development and applications of novel DGT passive samplers for measuring 12 per- and polyfluoroalkyl substances in natural waters and wastewaters. Environmental Science & Technology 55 (14), 9548-9556.