Supporting Information for

Validation and Application of the Diffusive Gradients in Thin-Films Technique for In Situ Measurement of β-Blocker Drugs in Waters and Sediments

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1. Method and Materials

1.1. Chemicals and Regents

High purity standards were purchased from Sigma-Aldrich (https://www.sigmaaldrich.com/). The physicochemical properties of the target compounds and IS are listed in the Table S1. Stock solutions at 1000 mg/L were made in pure methanol (MeOH). MeOH and acetonitrile (ACN) were purchased from Merck (Germany). HLB resin was purchased from Waters (USA). NaCl, NaOH, HCl and humic acid (fulvic acid ≥ 90%) were all purchased from Aladdin, China.

The DGT moludings were purchased from DGT Research Ltd (China). 7 membrane filters, namely polyvinylidene fluoride (PVDF, 0.14 mm), polyether sulfone (PES, 0.14 mm), GH polypro (GHP, 0.114 mm), NyLon (0.14 mm), mixed cellulose ester (MCE, 0.14 mm), cellulose acetate fiber (CA) filter membranes were all purchased from NewStar (Hangzhou, China), polytetrafluoroethylene filter membranes (PTFE, 0.065 mm) were obtained from PALL (UK).

1.2. Possible Adsorption by Diffusive Gels, Filter Membranes and DGT Mouldings

PA diffusive gels and 7 filter membranes were immersed individually in 10 mL of mixed target compound solutions at 50 μg/L while DGT mouldings (cap and base) were exposed in 50 mL. All materials were soaked in MQ water as blanks, and mixed compounds only were served as control samples. All the solutions were shaken in a water bath (100 r/min) at 25℃ for 18 hr. The concentrations of target compounds before and after shaking were measured to calculate the possible adsorption of target compounds on these materials.

1.3. Assemble of DGT probes for sediment samples

A DGT probe consisted of four layers from bottom to top: a rectangular filter membrane to prevent the binding gel from sticking to the backing plate, a binding gel, a PA diffusive gel, and another filter membrane to protect the gels. These four layers are held together by ABS probe moulding (purchased from DGT Research Ltd, UK) with an exposure window of 1.8 × 15 cm. They were de-oxidized overnight, prior to deployment.

1.4. Pre-test for DGT probes

A DGT probe with HLB binding gel was deployed in a well-stirred solution (0.01M NaCl, pH = 6.0±0.2) with known concentration of ATL for 24 hr. After deployment, all layers were cut from the exposure window with a razor blade and the diffusive gel and filter membrane were discarded. The binding gel was sliced into 5 mm strips and analysed following elution procedures described in the main test.

1.5. Sample preparation

After deployment, DGT binding gels were retrieved and extracted by ultrasonic bath with 10 mL ACN (strips cut from probes were extracted with 3 mL).

Water samples were divided into duplicate samples (1L each) before filtered through Whatman GF/F filters (47 mm, 0.7 μm), overlying waters and pore-waters were also filtered. HLB SPE cartridges were preconditioned with 10 mL MeOH and 10 mL MQ water, all water samples were added with 50 ng/L IS before loading to the cartridges at 1~2 drop/s. Then SPE cartridges were washed with 10 mL MQ water and vacuum dried for 30 min. The analytes on the cartridges were eluted with 10 mL ACN.

All the eluates (from laboratory and field samples) were blown to dryness under gentle N_2 stream, re-dissolved with 0.2 mL MeOH: MQ = 1: 9, then filtered with 0.2 μm syringe filters prior to analysis.

Table S1 Physicochemical properties of the target β-blockers

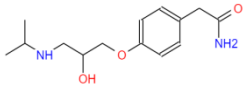
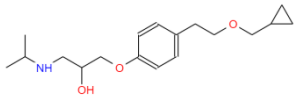
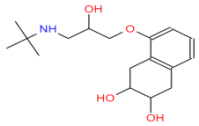
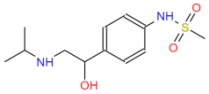
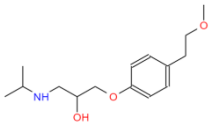
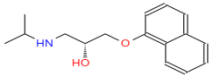
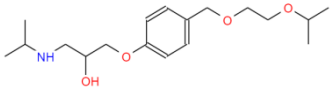
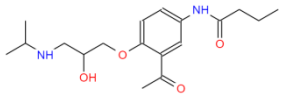
Compound	Abb.	CAS	MW	logKow	pKa	Formula	Structure
Atenolol	ATL	29122-68-7	266.3	0.16	9.58	$C_{14}H_{22}N_2O_3$	
Betaxolol	BTL	63659-18-7	307.4	2.81	9.21	$C_{18}H_{29}NO_3$	
Nadolol	NDL	42200-33-9	309.4	0.81	9.67	$C_{17}H_{27}NO_4$	
Sotalol	STL	3930-20-9	272.4	0.24	9.76	$C_{12}H_{20}N_2O_3S$	
Metoprolol	MTL	51384-51-1	267.4	1.88	9.56	$C_{15}H_{25}NO_3$	
Propranolol	PPL	525-66-6	259.4	3.48	9.45	$C_{16}H_{21}NO_2$	
Bisoprolol	BSL	66722-44-9	325.5	1.87	9.57	$C_{18}H_{31}NO_4$	
Acebutolol	ABL	37517-30-9	336.4	1.71	9.67	$C_{18}H_{28}N_2O_4$	

Table S2 MSMS parameters for target β-blockers

Compound	Precursor Ion	Product Ion	CE	DP
ATL	267.1	145.2	38.9	84.8
	267.1	190	26.6	84.8
BTL	308	116	27.75	110.69
	308	98.1	31	110.69
NDL	310.2	253.9	23.25	80
	310.2	201.1	32	80
STL	273.3	133	39	54.88
	273.3	213.1	25.12	54.88
MTL	268.3	116	27.63	33.87
	268.3	191	20.83	33.87
PPL	260.4	183	22.39	90
	260.4	116.3	24.23	90
BSL	326.4	115.9	28	90
	326.4	73.9	51	90
ABL	337.2	116.2	34.55	78.92
	337.2	98.1	29.94	78.92
ATR-d7	274	145	38.28	97
	274	190	27.01	97

Table S3 Elution efficiencies of target compounds

Compound	MeOH (%)	ACN (%)	5%NH_3 in MeOH (%)
ATL	56.91 ± 5.22	80.29 ± 3.05	106.20 ± 9.36
NDL	89.13 ± 5.47	87.94 ± 5.88	93.81 ± 7.65
STL	63.52 ± 8.60	89.22 ± 3.95	96.04 ± 5.15
BTL	67.86 ± 14.56	75.66 ± 6.47	90.51 ± 9.65
MTL	84.36 ± 4.32	78.16 ± 5.91	93.36 ± 6.85
PPL	54.17 ± 15.83	71.19 ± 1.73	89.37 ± 8.58
BSL	75.84 ± 8.85	77.88 ± 2.86	92.74 ± 9.85
ABL	89.31 ± 1.16	83.37 ± 1.32	90.93 ± 5.37

Table S4 Diffusion coefficients of 8 target β-blockers at test temperature (27.6°C, measured) and standard temperature (25°C, calculated)

Compound	*D* at 27.6°C (E-06 cm^2/s) (measured)	*D* at 25°C (E-06 cm^2/s) (calculated)
ATL	4.99	4.66
NDL	4.58	4.27
STL	5.25	4.90
BTL	4.24	3.95
MTL	5.26	4.90
PPL	5.36	5.00
BSL	4.28	4.00
ABL	4.95	4.61

Table S5 Detection limits (IDLs and MDLs) for DGT samples during lab and field deployments

Compound	IDL[a] (μg/L)	Lab sample MDL[b] (ng/L)	Field sample MDL[c] (ng/L)
ATL	0.23	1.55	0.22
NDL	0.08	0.68	0.10
STL	0.12	0.89	0.13
BTL	0.09	0.85	0.12
MTL	0.10	0.75	0.11
PPL	0.10	0.76	0.11
BSL	0.04	0.37	0.05
ABL	0.06	0.49	0.07

a: IDLs were calculated based on IDL = 3SD, where SD is the standard deviation from a measured concentration of standard (8 times)

b: Lab MDLs were calculated based on the 1-day deployment in the lab experiments under 25°C condition

c: Field MDLs were calculated according to 7-daydeployment in the field application under 25°C condition

Table S6(a). Water parameters of the 7 sampling sites.

Sites	pH	DOC (mg L^{-1})	T (℃)
S1	8.17±0.05	5.59±0.01	10.2±0.4
S2	8.08±0.04	7.84±0.03	12.4±0.5
S3	7.92±0.06	12.40±0.04	14.4±0.6
S4	8.14±0.07	6.46±0.06	13.5±1.1
S5	8.14±0.02	6.09±0.02	12.3±0.8
S6	8.10±0.06	5.41±0.05	9.6±0.5
S7	8.20±0.09	13.31±0.04	11.2±0.3

Table S6(b). Parameters of the sediment sample (overlying water).

Sites	pH	DOC (mg L^{-1})	T (℃)
S1	7.02±0.08	13.62±0.01	15.2±0.2

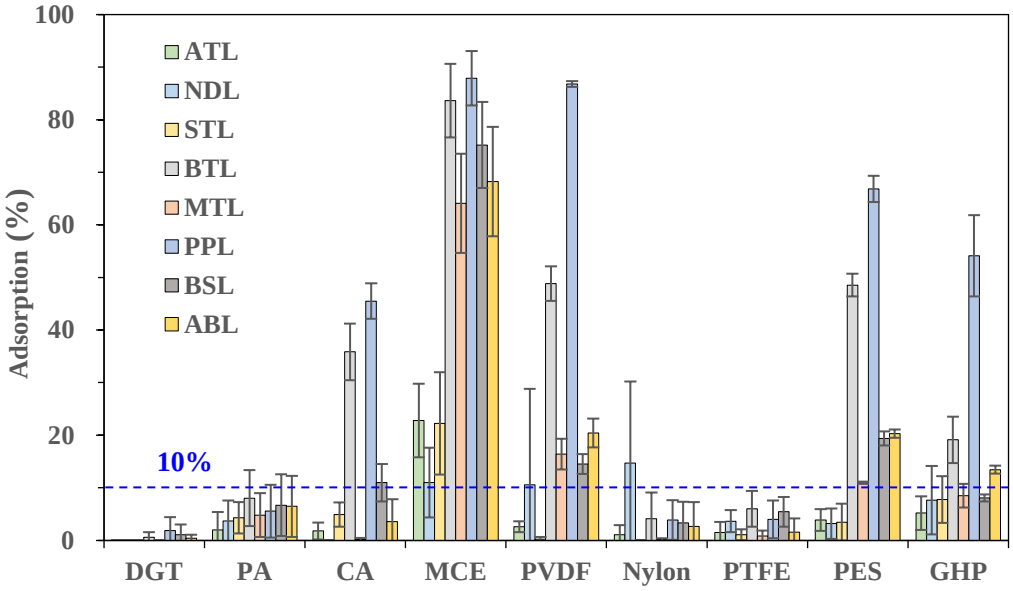


Figure S1 Adsorption of target β-blockers onto DGT mouldings, agarose diffusive gels and 7 filter membranes. Error bars were calculated from the standard deviations of three replicates.

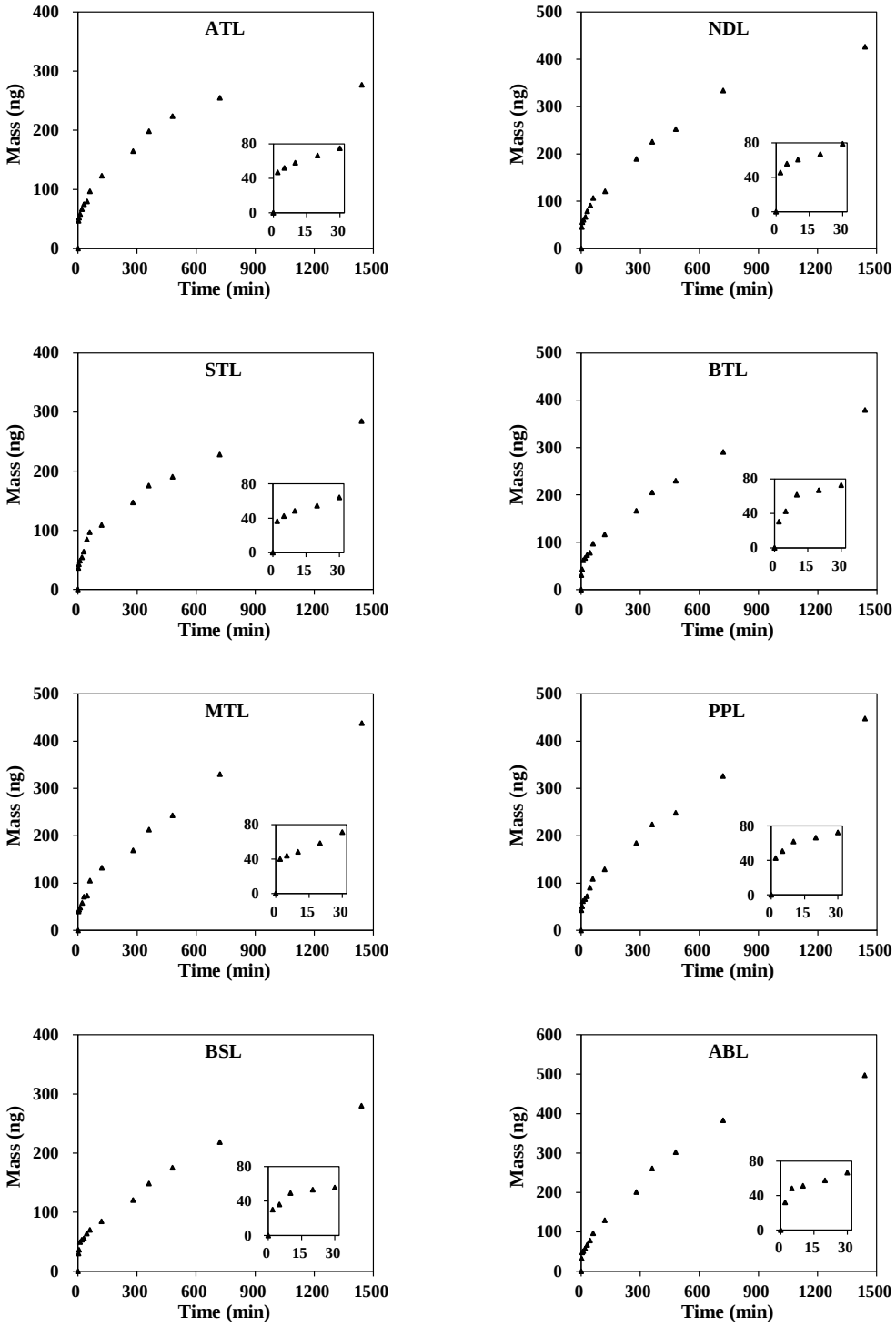


Figure S2 Binding kinetics of target compounds by binding gels.

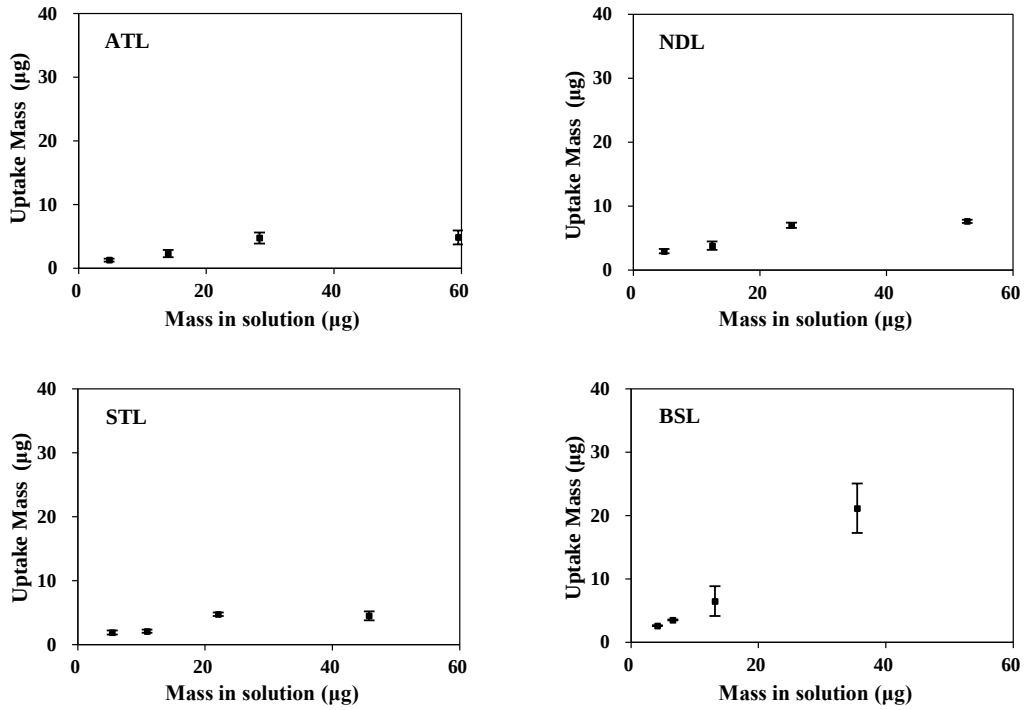


Figure S3 Effective binding capacities of 4 target compounds by DGT devices.

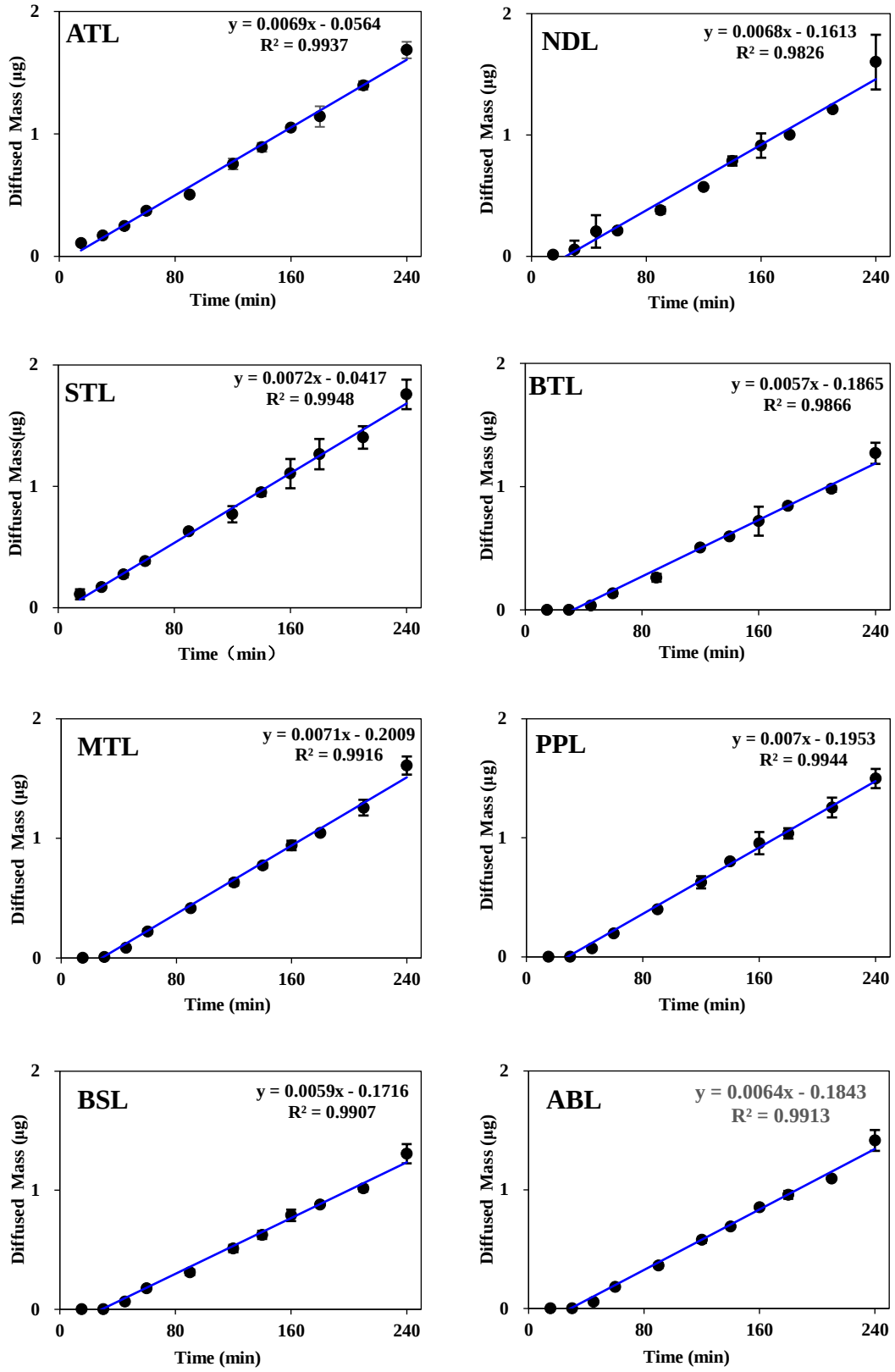


Figure S4 Masses of the target β-blockers diffused through the diffusion layer (a 0.78 mm PA diffusive gel and a 0.065 mm PTFE filter membrane) at different times (0 – 240 min) in the diffusive cell. (pH = 6.4 ± 0.2, IS = 0.01 mol/L, T = 27.6 ± 0.1 ℃).

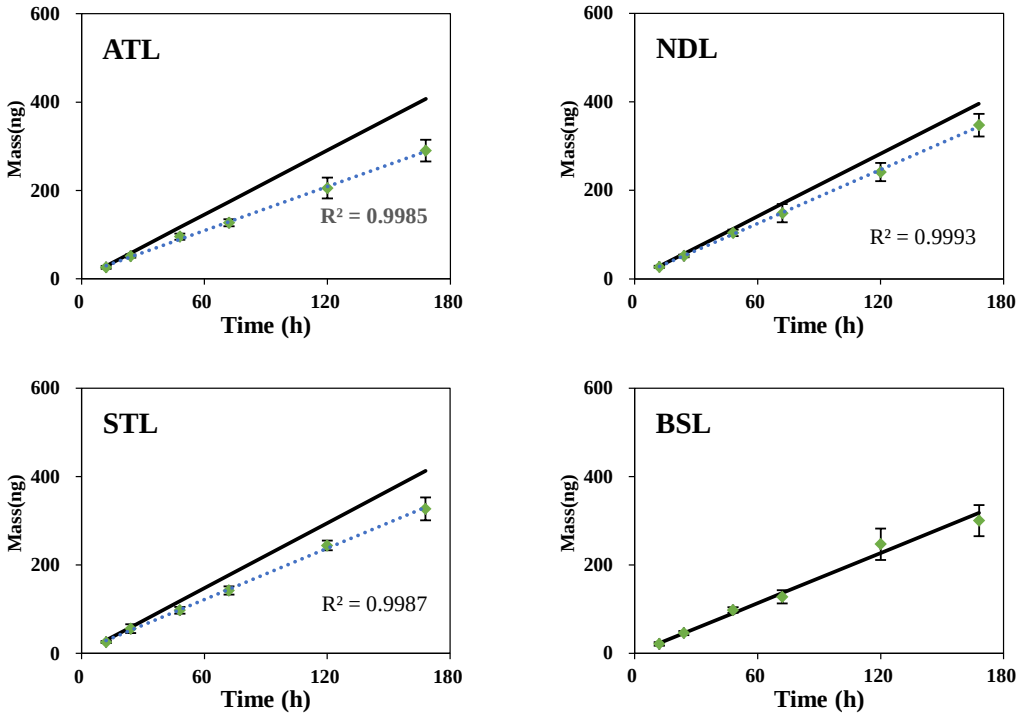


Figure S5 Measured masses of 4 target β-blockers accumulated onto DGT devices for different times (pH = 6.3 ± 0.2, 0.01 mol/L NaCl, T = 20 ± 0.6°C). The solid lines are theoretical lines.

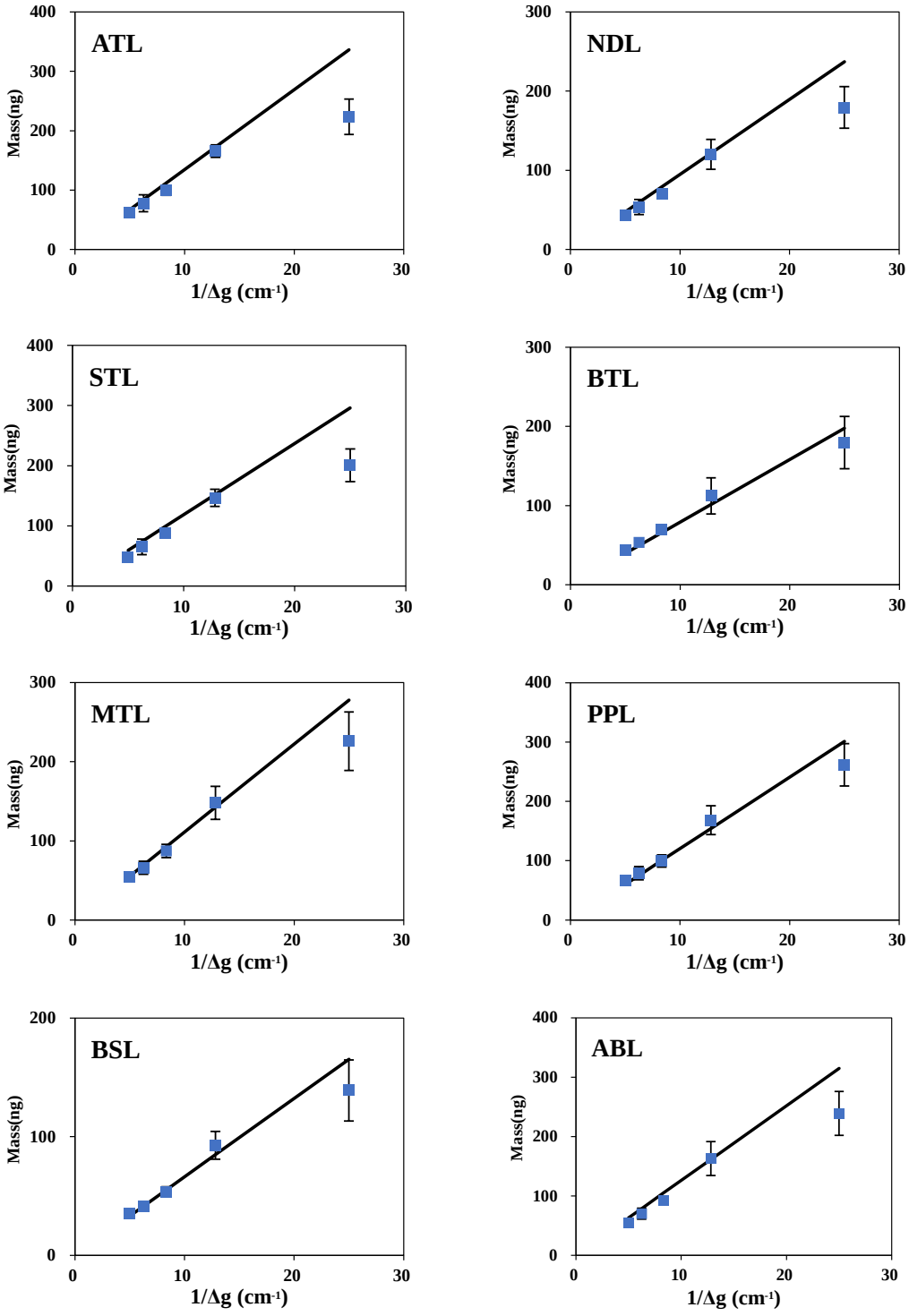


Figure S6 Measured masses of target β-blockers accumulated onto DGT devices with different diffusion layer thicknesses (pH = 6.5 ± 0.1, 0.01 mol/L NaCl, T = 21 ± 0.2°C). The solid lines are theoretical lines.



Figure S7 Map of sampling sites for deployment in rivers.

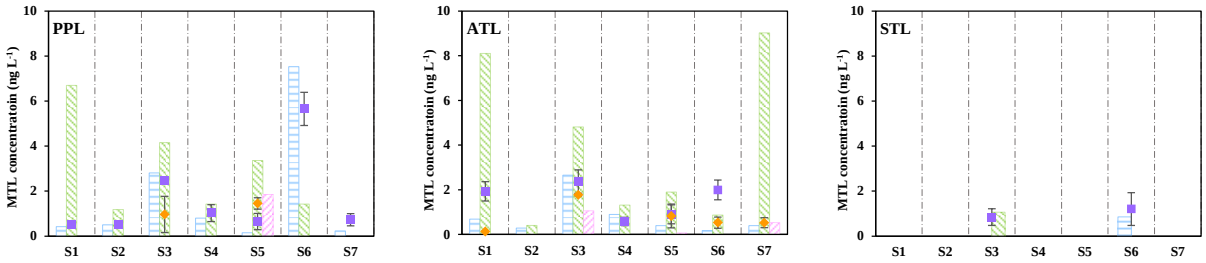
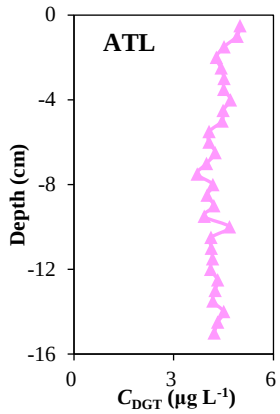


Figure S8 Concentrations of PPL, ATL and STL detected at 8 sampling sites (bars: grab samples collected on different days (blue: Day 1; green: Day 7; pink: Day 14); dots: DGT samples deployed for different time length (purple dots: 7 days; orange dots: 14 days)).



$C_{solution}$ (μg L^{-1})	C_{DGT} (μg L^{-1})	RSD.
4.63	4.30	6.68%

Figure S9 Concentration profile of ATL measured using a DGT probe in a well-stirred solution with average concentrations and relative standard deviation (μg/L).

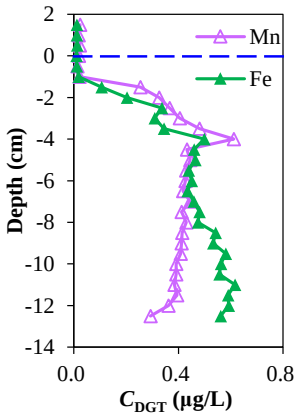


Figure S10 Mn and Fe concentration profiles with depths in the sediment core measured using DGT probe. Blue dash lines is the SWI.