Supporting Information

Preparation of water samples by MIP-DGT and grab sampling for HPLC-MS/MS analysis

After DGT deployment, binding gels were taken out from the devices and soaked in 2 mL methanol-acetic acid (*v/v*: 9/1), shaken twice for 12 h. The elutes were collected and spiked with 50 ng internal standards (sulfadiazine-d_6 and ciprofloxacin-d_8), then blown with N_2 to near dryness and re-dissolved in 1 mL 0.1% methanoicacid/ammonium formate–acetonitrile (*v/v*: 85/15). After filtration with 0.22 μm PTFE filter, the eluents were determined by HPLC-MS/MS.

Water samples were collected in 2 L PP bottle and transported to laboratory and treated within 24 h. The samples were filtered through 0.45 μm glass fiber membrane and adjusted to pH = 2.5. The samples (500 mL) were added with 50 ng internal standards (sulfadiazine-d_6 and ciprofloxacin-d_8) and 200 mg Na_2EDTA and then were extracted using Waters OASIS^{TM} HLB cartridges. Before loading samples, the cartridges were first pretreated with 10 mL methanol, 10 mL Milli-Q water and 10 mL Milli-Q water (pH 2.5). The samples were introduced to the cartridges by vacuum filtration at a flow rate of 10 mL/min. After loading the samples, the sample bottles were washed three times using Milli-Q water, and then passed through the cartridges. Finally, the cartridges were rinsed with 10 mL Milli-Q water and allowed to dry for 30 min under vacuum, and then were eluted by 12 mL methanol. The eluates were evaporated to near dryness under a gentle stream of nitrogen and re-dissolved in 1 mL of 0.1% methanolic acid/ammonium formate–acetonitrile (v/v: 85/15). The solutions were filtered with 0.22 μm PTFE filter and analyzed by HPLC-MS/MS.

HPLC and HPLC-MS/MS analysis

HPLC analysis was analyzed by the Shimadzu LC-16 (Japan) with an ultraviolet detector using a Hypersil ODS2 column (5 μm, 4.6 mm × 250 mm, Agilent, China). The column temperature maintained 30℃ at a flow rate of 1 mL/min. The detection wavelength was 278 nm for SAs, 284 nm for FQs. The mobile phases were MQ water with 0.1% trifluoroacetic acid (A phase) and acetonitrile (B phase). The gradient program was as followed: 0.1–7 min, 30% B; 7–7.3 min, 30% to 25% B; 7.3–8 min, 25% to 20% B; 8–9 min, 20% to 15% B; 9 to 14 min, 15% B.

HPLC-MS/MS analysis was performed by an Agilent 6410B triple quadrupole LC/MS (USA) equipped with and an ESI ionization source. A Waters Xterra C18 separation column (100 mm × 2.1 mm, 3.5 μm, China) was used to separate targets. The mobile phases consisted of 0.1% methanoicacid-ammonium formate (A phase) and acetonitrile (B phase). The gradient program was as followed: 0.1–8 min, 15% to 60% B; 8–10 min, 60% B; 10–18 min, 60% to 15% B. The flow rate was 0.25 mL/min and the injection volume was 5 μL. MS parameters included: nebulizer pressure of 25 psi, capillary voltage of 4000 V, gas temperature of 350℃ and gas flow rate of 8 mL. The retention time, precursor ions, product ions, collision energy and fragmentor voltage were given in Table S3.

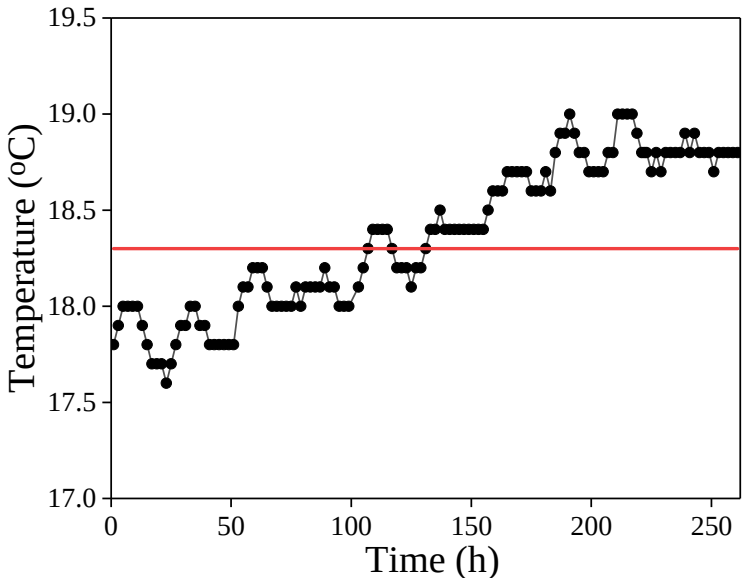


Fig. S1 Temperatures of the WWTP effluent measured by a temperature logger. The red solid line represents the average value (18.3℃)

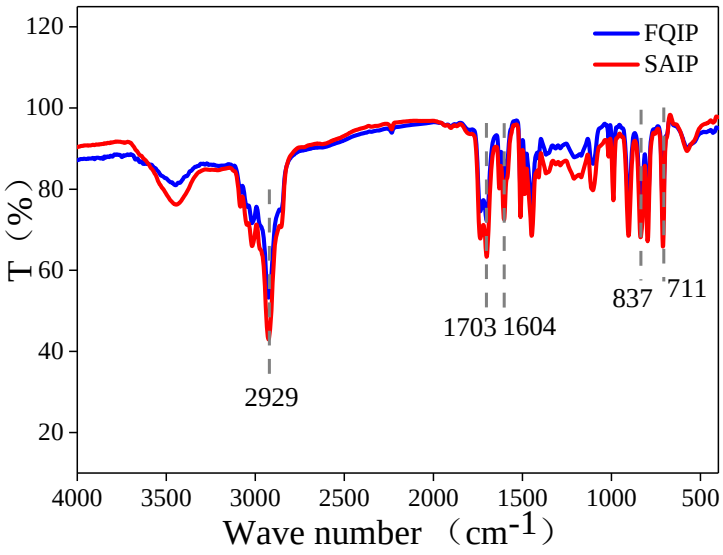
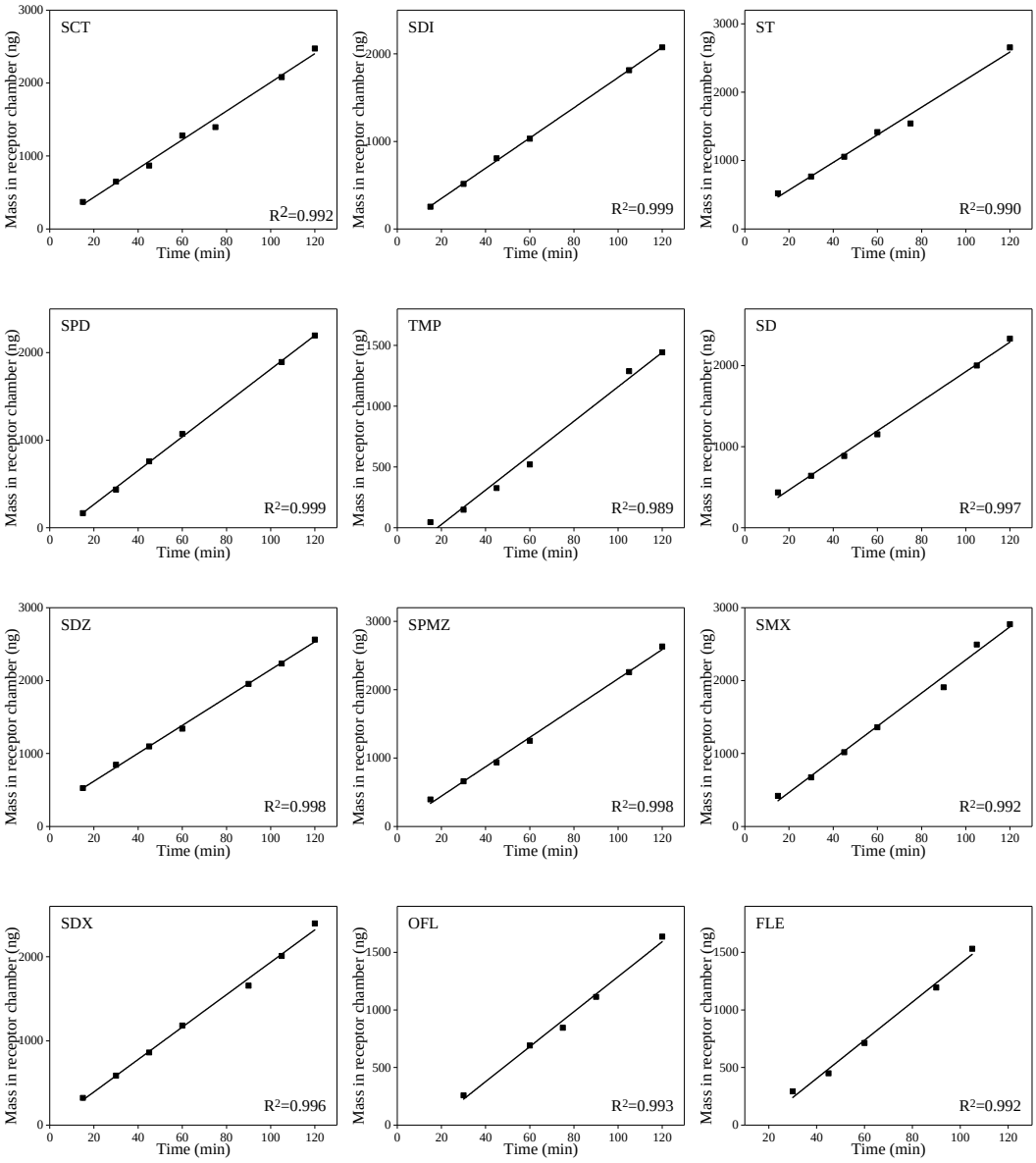


Fig. S2 Fourier Transform Infrared spectra of FQIP and SAIP


SCT
R2=0.992
SDI
R2=0.999
ST
R2=0.990
SPD
R2=0.999
TMP
R2=0.989
SD
R2=0.997
SDZ
R2=0.998
SPMZ
R2=0.998
SMX
R2=0.992
SDX
R2=0.996
OFL
R2=0.993
FLE
R2=0.992
Mass in receptor chamber (ng)
Time (min)

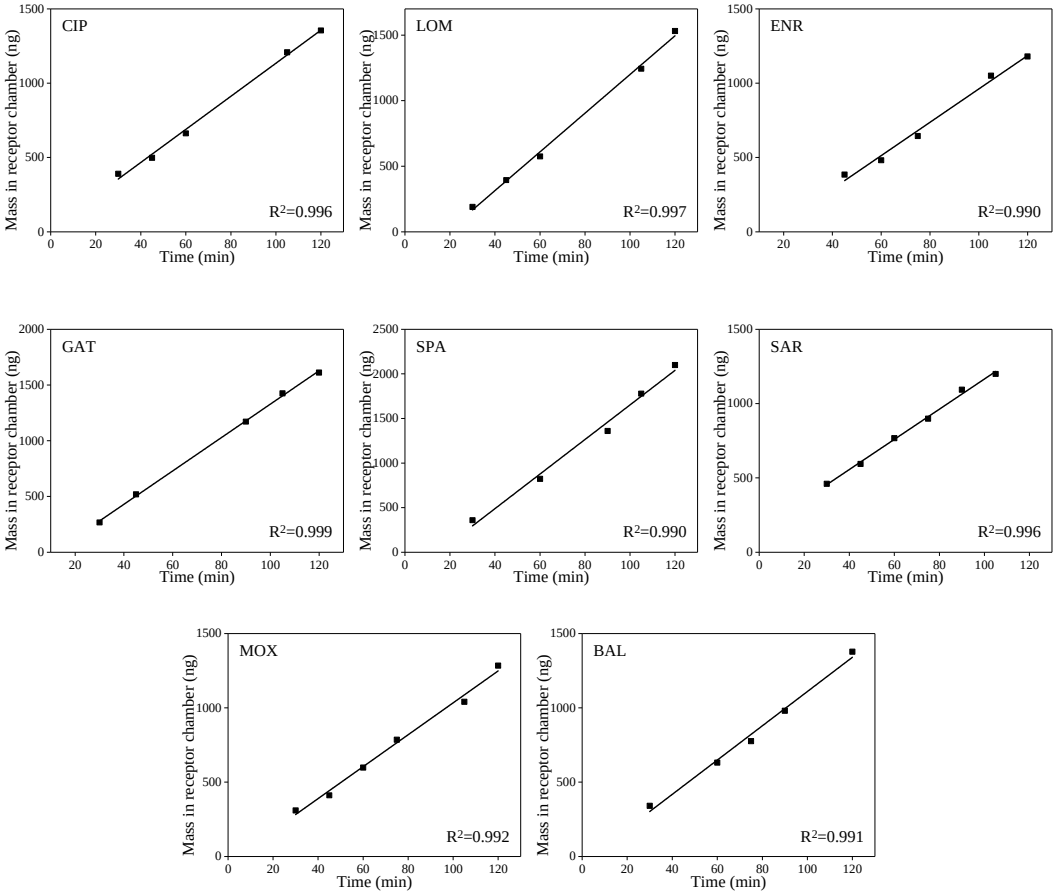


Fig. S3 Plot of masses of antibiotics in the receptor chamber versus time in the diffusion coefficient measurements (25℃)

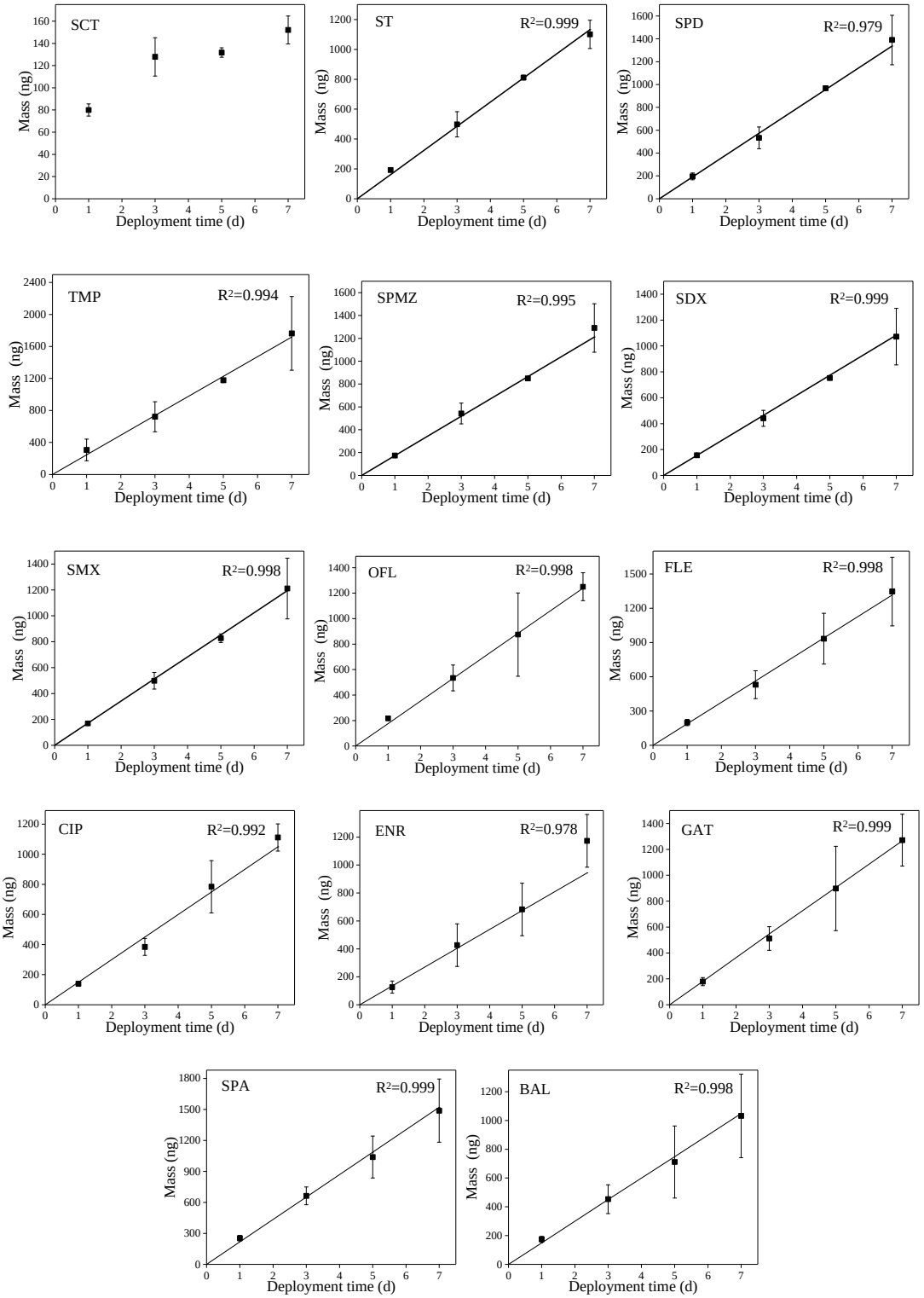


Fig. S4 Masses of 20 antibiotics accumulated by MIP-DGT (pH 6.3 ± 0.2, 10 mM NaCl) at different deployment time. Solid line is theoretical lines predicted by the DGT Eq. (1). Error bars represented the standard deviations of triplicates

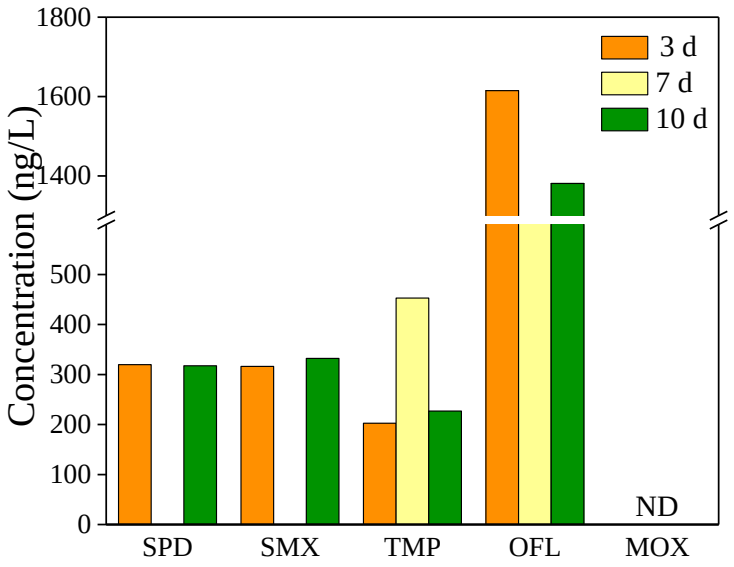


Fig. S5 The concentrations of antibiotics in the influent of WWTP by grab sampling during 3, 7, 10 days deployment

Table S1 Physical-chemical properties of target antibiotics

Chemicals CAS. NO*	Molecular formula*	MW*	Solubility* (mg/L)	pK_a*	Log K_{ow}
Sulfamethoxazole	$C_{10}H_{11}N_3O_3S$	253.28	380	1.39	0.89
723-46-6				5.81	
Sulfadiazine	$C_{10}H_{10}N_4O_2S$	250.28	800	1.1	–0.09
68-35-9				6.81	
ulfamerazine	$C_{11}H_{12}N_4O_2S$	264.3	500	1.1	0.14
127-79-7				7.35	
Sulfadimidine	$C_{12}H_{14}N_4O_2S$	278.33	310	1.69	0.89
57-68-1				7.89	
Sulfapyridine	$C_{11}H_{11}N_3O_2S$	249.29	770	2.13	0.35
144-83-2				8.54	
Sulfathiazole	$C_9H_9N_3O_2S_2$	255.32	1900	2.19	0.05
72-14-0				7.24	
Sulfacetamide	$C_8H_{10}N_2O_3S$	214.24	15000	0.93	–0.96
144-80-9				5.43	
Sulfadoxine	$C_{12}H_{14}N_4O_4S$	310.33	400	2.18	0.7
2447-57-6				6.16	

Sulfamethoxypyridazine	$C_{11}H_{12}N_4O_3S$	280.3	1100	2.04	0.32
80-35-3				7.19	
Trimethoprim	$C_{14}H_{18}N_4O_3$	290.32	490	7.04	0.91
738-70-5					
Ofloxacin	$C_{18}H_{20}FN_3O_4$	361.37	69	5.19	–2
82419-36-1				7.37	
Ciprofloxacin	$C_{17}H_{18}FN_3O_3$	331.34	43	6.43	0.28
85721-33-1				8.68	
Enrofloxacin	$C_{19}H_{22}FN_3O_3$	359.39	19	6.43	0.7
93106-60-6				7.76	
Sarafloxacin	$C_{20}H_{17}F_2N_3O_3$	385.36	230	6.17	1.07
98105-99-8				8.68	
Fleroxacin	$C_{17}H_{18}F_3N_3O_3$	369.34	41	–0.54	0.24
79660-72-3				7.15	
Lomefloxacin	$C_{17}H_{19}F_2N_3O_3$	351.35	24	–0.25	–0.3
98079-51-7				8.57	
Gatifloxacin	$C_{19}H_{22}FN_3O_4$	375.39	19	6.43	0.5
112811-59-3				8.72	
Sparfloxacin	$C_{19}H_{22}F_2N_4O_3$	392.4	2.9	6.42	0.12
110871-86-8				8.59	
Moxifloxacin	$C_{21}H_{24}FN_3O_4$	401.43	2.7	6.43	0.95
151096-09-2				10.63	
Balofloxacin	$C_{20}H_{24}FN_3O_4$	389.42	6.2	6.44	0.99
127294-70-6				9.88	

Notes: *Data were collected from SciFinder Scholar; Log K_{ow} were obtained from the website of ChemSpider

Table S2 COD, pH, and flow rate of effluent of the WWTP during the DGT deployment

Sites	Time	COD (mg/L)	pH	Flow (m^3/d)
influent	05/27/2019	214.70	7.44	4089.44
	05/30/2019	197.77	7.60	3934.03
	03/06/2019	165.51	7.78	3704.86
	06/06/2019	163.48	7.86	3878.47
effluent	05/27/2019	12.33	5.17	3573.39
	05/30/2019	11.23	5.10	3543.40
	03/06/2019	10.45	5.19	3520.83
	06/06/2019	12.67	5.15	3713.54

Table S3 MS/MS parameters for the determination of 20 antibiotics

Compounds	Precursor ions	Product ions	Fragment voltage (V)	Collision energy (V)	Ret Time (min)
SMX	254	155.8	105	13	6.788
SDI	251.2	156.1	110	13	2.352
SD	265	156.0	110	13	3.133
SDZ	279	156.1	102	13	4.096
SPD	250.3	155.9	110	13	2.824
ST	256	155.9	92	13	2.623
SCT	214.9	156.0	110	15	2.109
SDX	311	155.9	110	15	6.502
SPMZ	281.1	156.0	110	15	4.552
TMP	291	230.0	165	21	3.008
OFL	362.2	318.0	154	17	3.520
CIP	332.1	288.1	100	15	3.906
ENR	360	316.0	180	17	5.205
SAR	386	298.9	110	30	6.276
FLE	370.2	326.2	110	20	3.614
LOM	352	265.2	110	20	4.494
GAT	376.3	261.1	110	32	5.914
SPA	393.2	292.0	110	26	6.397
MOX	402.2	384.1	145	20	6.861
BAL	390.2	359.2	120	15	6.963
SDI-d_6	257.1	162.1	105	12	2.440
CIP-d_8	340.2	235.1	105	30	4.223

Table S4 LODs and LOQs of 20 antibiotics by HPLC-MS/MS and method detection limits (MDLs) of seven days MIP-DGT deployment coupled with HPLC-MS/MS

Compounds	LOD (μg/L)	LOQ (μg/L)	MDL (μg/L)	DGT blank
SMX	0.293	0.810	0.004	ND
SDI	0.152	0.316	0.003	ND
SD	0.084	0.401	0.001	ND
SDZ	0.120	0.541	0.002	ND
SPD	0.222	0.891	0.003	ND
ST	0.593	1.716	0.007	ND
SCT	1.667	4.701	0.021	ND
SDX	0.106	0.434	0.002	ND
SPMZ	0.133	0.442	0.002	ND
TMP	0.124	0.366	0.002	ND
OFL	0.203	0.840	0.003	ND
CIP	0.338	0.994	0.007	ND
ENR	0.541	1.463	0.012	ND
SAR	0.133	0.417	0.003	ND
FLE	0.187	0.744	0.003	ND
LOM	0.240	0.702	0.005	ND
GAT	0.338	0.815	0.005	ND
SPA	0.063	0.183	0.001	ND
MOX	0.382	0.964	0.009	ND
BAL	0.321	1.035	0.006	ND

Notes: ND means no detected

Table S5 Fitting parameters of Langmuir equations for OFL on FQIP and SMX on SAIP

Analytes	Langmuir		
	b (L/mg)	Q_0 (mg/g)	R^2
FAIP	0.0467	29.7	0.997
SAIP	0.132	88.5	0.998

Notes: Langmuir equation: $C_e/q_e = 1(q_m \cdot b) + C_e/q_m$, where q_e and q_m were the adsorption amount (mg/g) at equilibrium and the maximum capacity, respectively, *Ce* was the equilibrium concentration (mg/L), *b* is the Langmuir constant, and *n* was the Freundlich exponent

Table S6 Elution efficiencies (%) of 20 antibiotics from MIP binding gels eluted by methanol-acetic acid (v/v = 9:1)

Compounds	Elution efficiencies (%)	Compounds	Elution efficiencies (%)
SMX	99.02 ± 12.76	OFL	90.01 ± 4.48
SDI	105.98 ± 11.51	CIP	90.91 ± 2.72
SD	96.88 ± 12.54	ENR	123.37 ± 4.34
SDZ	106.36 ± 10.23	SAR	114.60 ± 10.59
SPD	116. 63 ± 15.68	FLE	97.07 ± 1.47
ST	101.48 ± 14.04	LOM	110.48 ± 9.77
SCT	144.74 ± 100.51	GAT	90.88 ± 8.56
SDX	100.02 ± 8.88	SPA	98.49 ± 1.58
SPMZ	99.46 ± 11.03	MOX	116.42 ± 10.10
TMP	144.44 ± 22.00	BAL	108.28 ± 12.00