Lancaster Environment Centre
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Fate of Emerging Organic Contaminants in Chinese Wastewater Treatment Plants

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Submitted for the degree of Doctor of Philosophy

To my lovely daughter and wife, Shi-Ying Chen and Yang Liu

Abstract

There has been increasing concern about the widespread occurrence of emerging organic contaminants (EOCs) in the aquatic environment which could pose potential risks to humans and ecosystems. Wastewater treatment plants (WWTPs) are significant sources and major routes of EOCs entering the environment. There is therefore a need to study the fate of EOCs in WWTPs to improve the risk assessment for these EOCs. In this thesis, the passive sampling technique of diffusive gradients in thin-films (DGT) for *in situ* measurement of selected EOCs in water was developed in the laboratory and validated under the real world condition-a WWTP. This sampler was then employed to study the occurrence and removal efficiencies of EOCs in Chinese WWTPs, as China represents a significant and growing market for many of these chemicals.

A novel DGT technique was developed for *in situ* measurement of EOCs in water, with hydrophilic-lipophilic-balanced (HLB) resin as the binding agent and agarose gel as the diffusion layer. The performance of DGT sampler (indicated by ratio of DGT-measured concentrations (C_{DGT}) to the directly-measured concentration (C_b), the ratio of C_{DGT}/C_b ranged from 0.9 to 1.1 indicating the excellent performance of DGT) in different pH, ionic strength and dissolved organic matter contents was tested with 11 chemicals and found to be relatively independent of pH (3.5-9.5), ionic strength (0.001-0.1 M) and dissolved organic matter (0-20 mg L^{-1}). Time and diffusion layer thickness dependence experiments confirmed the principle of DGT for accumulated chemicals consistent with theoretical predictions.

The performance comparison of three types of resins (HLB, XAD18 and Strata-XL-A) was undertaken. Resin properties and the interactions of functional groups between the resin and chemicals controlling the uptake of EOCs for DGT sampler were evaluated by comparing the uptake capacities and the kinetics of the test chemicals among three resins. The study in the laboratory, which is similar to above section for three types of DGT devices with HLB, XAD18 and Strata-XL-A resins as the binding gels, confirmed the potential application of DGT principle for *in situ* measurement of EOCs in water.

This DGT sampler was then compared with active sampling approaches, auto-sampling and grab-sampling in a WWTP. This study showed that the DGT sampler can continuously uptake the majority of detected EOCs in wastewater for 7-18 days. The time-weighted average

concentrations measured by DGT were found to be comparable with the results delivered from the auto-samplers, showing similar concentrations and patterns. The effect of diffusive boundary layer was estimated, and was found to be relatively limited and much less compared with other passive samplers, demonstrating the advantage of DGT sampler. The field validation confirmed applicability of DGT sampler for studying the fate of EOCs in the wastewater.

Before application of the DGT sampler into a large scale of fate study in Chinese WWTP, a sensitive analytical method was developed for simultaneous determination of target EOCs in surface water and wastewater. This method was optimised from solid-phase extraction (SPE) procedures to liquid chromatography-mass spectrometer (LC-MS) analysis, and was demonstrated to provide reliable data for the samples with complex matrix and low enough detection limits for EOCs in the water. This analytical method could perform similarly or even better to some related studies for detection of the EOCs in wastewater.

DGT devices with HLB resin gels were then applied to 10 WWTPs in China for studying the occurrence and removal of EOCs. All target EOCs could be found in the raw influent and majority of them (18 of 20) could still be detected in the final effluent. Removal efficiency of the EOCs varied, showing the performance of different treatment technology/processes on the EOCs removal in wastewater. The primary and secondary treatment units contributed to the most removal of the EOCs. This demonstrated that DGT sampler can be an effective and simple tool to study in fate of EOCs in wastewater.

This research programme has shown that DGT sampler is an effective tool for studying the fate of wide range of emerging organic chemicals in the aquatic environment and assessing their risk/ toxicity of EOCs to the human and ecosystem.

Acknowledgements

There is no way to complete my PhD study without supporting from my supervisors, family, colleagues, friends and all the people who care about me. No words could express my gratitude to them all.

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List of Papers

This thesis contains a number of papers that are published, in press, submitted, have been prepared for submission to appropriate journals or in preparation. They are listed below together with brief details of the contribution made by the candidate and the co-authors.

I Chen, W., Chen, C-E., Price, O.R., Pan, S-H., Ying, G-G., Li, H., Jones, K.C., Sweetman, A.J., Zhang, H. Development of DGT passive sampling technique for *in situ* measurements of trace organic chemicals discharged in household wastewater. Ready for submitting to *Environmental Science & Technology*.

Wei Chen designed the experiments, conducted the data analysis and wrote the manuscript, Chang'er Chen gave some suggestions on the experiment preparation and data processing, Suhong Pan helped for some experiment preparation, Oliver R. Price, Guang-Guo Ying, Hong Li, Kevin C. Jones and Andy J. Sweetman gave the comments and helped to revise the manuscript, Hao Zhang gave suggestion on the experiment preparation and data interpretations, and majorly revised the manuscript.

II Chen, W., Price, O.R., Sweetman, A.J., Jones, K.C., Zhang, H. Comparative evaluation of DGT samplers with different binding resins for *in situ* measurement of trace organic chemicals in waters. In preparation.

Wei Chen designed the experiments conducted the data analysis and wrote the manuscript, Oliver R. Price, Kevin C. Jones and Andy J. Sweetman gave the comments and helped to revise the manuscript, Hao Zhang gave suggestion on the experiment preparation and data interpretations, and majorly revised the manuscript.

III Chen, W., Huang, H-F., Chen, C-E., Qi, S-H., Price, O.R., Zhang, H., Jones, K.C., Sweetman, A.J. Simultaneous determination of 20 trace organic chemicals in waters by solid-phase

extraction (SPE) with triple-quadrupole mass spectrometer (QqQ-MS) and hybrid quadrupole Orbitrap high resolution MS (Q-Orbitrap-HRMS). *Chemosphere*. **2016**, 163, 99-107.

Wei Chen designed and conducted the experiments, field sampling, instrumental analysis, and manuscript writing, Huanfang Huang provided assistants on field sampling in China and Q-Orbitrap-HRMS operation, Chang'er Chen helped on the experiment preparation and QqQ-MS operation and provided comments on the manuscripts, Shihua Qi, Oliver R. Price, Hao Zhang and Kevin C. Jones provided comments and helped to revise the manuscript, Andy J. Sweetman gave suggestion on the experiment preparation, data interpretations, and provided comments and majorly revised the manuscript.

IV Chen, W., Li, Y-Y., Price, O.R., Zhang, H., Sweetman, A.J., Jones, K.C. Validation of DGT Technique for Trace Organic Chemicals in Waters. Prepared for submission.

Wei Chen designed and undertook the field work, conducted sample pre-treatment, instrumental and data analysis, and wrote the manuscript, Yangying Li helped in the field work and sample preparation, Oliver R. Price and Andy J. Sweetman gave the comments and helped to revise the manuscript, Hao Zhang and Kevin C. Jones gave suggestion on the experiment preparation and data interpretations and majorly revised the manuscript.

V Chen, W., Huang, H-F., Zhao W-X., Qi, S-H., Chen, J-W., Price, O.R., Zhang, H., Sweetman, A.J., Jones, K.C. Fate of Trace Organic Chemicals at Chinese Wastewater Treatment Plants (WWTPs): Occurrence and Removal Based on DGT Techniques. In preparation.

Wei Chen designed and conducted the field sampling, sample pre-treatment and instrumental analysis and manuscript writing, Huanfang Huang and Wenxing Zhao provided helps on sample collection and pre-treatment, Shihua Qi and Jingwen Chen helped to access the WWTPs, provided facilities for sampling and sample pre-treatment, Oliver R. Price, Hao Zhang and Andy J. Sweetman gave the comments and helped to revise the manuscript, Kevin C. Jones gave suggestions on field sampling design, result interpretations and majorly revised the manuscript.

List of Appendices

Appendix I **Co-authored article:** Chen, C-E., Chen, W., Ying, G-G., Jones, K.C., Zhang, H. *In situ* measurement of solution concentrations and fluxes of sulfonamides and trimethoprim antibiotics in soils using o-DGT. *Talanta*, **2016**, 132: 902-908.

Appendix II **Abstract for 23rd SETAC Europe Meeting:** Chen, W., Chen, C.-E., Zhang, H., Jones, K.C., Ying, G.-G., Xu, N., Price, O.R., Li, H., Sweetman, A.J. A passive sampler for *in situ* measurement of pharmaceutical and personal care ingredients in waters. *23rd Annual Meeting of the Society of Environmental Toxicology and Chemistry (SETAC Europe)*. Glasgow, UK. May 12~16, 2013

Appendix III **Abstract for Conference on DGT and the Environment:** Chen, W., Chen, C-E., Zhang, H., Price, O.R., Sweetman, A., Jones, K.C., Li, H. Performance Comparison on Three Resins of o-DGT for *in-situ* PPCP Measurement in Waters. *Conference on DGT and the Environment*. Lancaster, UK. July 9~11, 2013.

Appendix IV **Abstract for DGT Conference 2015:** Chen, W., Li, Y-Y., Price, O.R., Chen, C-E., Li, H., Zhang, H., Sweetman, A.J., Jones., K.C. Field evaluation of o-DGT for *in situ* measurement of pharmaceuticals and personal care ingredients in wastewater. *DGT Conference 2015*. Donostia-San Sebastián, Span. September 28~October 1, 2015.

Abbreviations

A	Exposure window area, cm^2
ACN	Acetonitrile
AMPA	Aminomethyl phosphonic acid
ANOVA	Analysis of variance
A2/O	Anaerobic/anoxic/oxic
A/O	Anaerobic/oxic
AS	Activated sludge
BAF	Biological aeration filter
BEP	Benzylparaben
BHA	Butylated hydroxyanisole
BHT	Butylated hydroxytoluene
BPA	Bisphenol-A
BPB	Bisphenol-B
BPF	Bisphenol-F
BPs	Bisphenols
BUP	Butylparaben
CAS	Chemical Abstracts Service
C_b	Analyte concentration in the bulk solution
C_{DGT}	Water concentration measured by DGT
4-CP	4-chlorophenol
C_S	Analyte concentration in the passive sampler
C_W	Analyte concentration in the aqueous environment
δ	Thickness of diffusive boundary layer, mm
Δg	Thickness of the diffusive layer, mm
D_{25}	Diffusion coefficient of analyte at 25 ℃, 10^{-6} cm^2 s^{-1}
DAD	photodiode array detector
DBL	Diffusive boundary layer
D_e	Diffusion coefficient of analyte, 10^{-6} cm^2 s^{-1}
DES	Diethylstilbestrol
DGT	Diffusive gradients in thin-films
DOM	Dissolved organic matter
D_T	Diffusion coefficient of analyte at temperature T, 10^{-6} cm^2 s^{-1}
E1	Estrone
E2	β-estradiol

E3	Estriol
EA	Ethyl acetate
EE2	17α-Ethinylestradiol
EOCs	Emerging organic contaminants
EQSs	Environmental quality standards
ESI	Electrospray ionisation
ETP	Ethylparaben
EUSES	European Union System for the Evaluation of Substance
h	Hour
H-bonding	Hydrogen bonding
HEP	Heptyl paraben
HLB	hydrophilic-lipophilic-balanced
HOCs	Hydrophobic organic chemicals
HPLC	High performance liquid chromatography
HRMS	High resolution mass spectrometer
IDLs	Instrument detection limits
IS	Ionic strength
ISs	Internal standards
K	Phase-water partition coefficient
k_1	Uptake rate constant
k_2	Offload rate constants
K_a	Acid dissociation constant
K_{ow}	Octanol–water partition coefficient
LC-MS	Liquid chromatography- mass spectrometer
M	Analyte mass accumulated in the passive sampler
MDLs	Method detection limits
MeOH	Methanol
MEP	Methylparaben
MEP of China	Ministry of Environment Protection of China
MIP	Molecularly imprinted polymers
MOHURD	Ministry of Housing and Urban-Rural Development
MQ	Milli-Q
NP	Nonylphenol
OD	Oxidation ditch
OPP	Ortho-phenylphenol
PES	Polyethenesulfone
PHBA	4-Hydroxybenzoic acid

PMG	Glyphosate
POCIS	Polar organic chemical integrative sampler
POCs	Polar organic chemicals
POPs	Persistent organic pollutants
PRCs	Performance reference compounds
PRP	Propylparaben
PWS	Passive water sampling
QA/QC	Quality assurance/quality control
Q_{max}	Maximum sorption capacity
Q-Orbitrap MS	Quadrupole-Orbitrap MS
QqQ-MS	Triple-quadrupole mass spectrometer
RAIDAR	Risk Assessment, IDentification, And Ranking model
REACH	Registration, Evaluation, Authorization, and Restriction of Chemicals
rpm	Revolutions per minute
RSD	Relative standard deviation
SBR	Requencing batch reactor
S/N	Ratio of signal/noise
SPE	Solid-phase extraction
SPMDs	Semipermeable membrane devices
SQ-MS	Single quadrupole mass spectrometer
R_S	Sampling rate
SXLA	Strata-XL-A
t	Time
T	Temperature
TCC	Triclocarban
TCS	Triclosan
TiO_2	Titanium dioxide
4-*t*-OP	4-*tert*-octylphenol
TOrCs	Trace organic chemicals
TRA	Targeted Risk Assessment
TSCA	Toxic Substances Control Act
TWA	Time-weight average
UHPLC	Ultrahigh performance liquid chromatography
UV	Ultraviolet
WWTPs	Wastewater treatment plants

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1. Introduction

1.1 Emerging Organic Contaminants (EOCs)

1.1.1 Introduction of EOCs

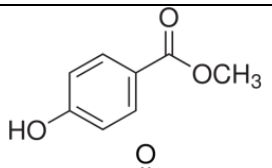
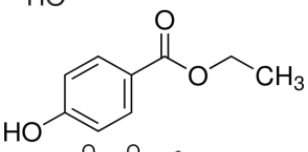
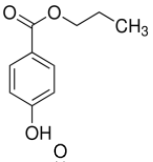
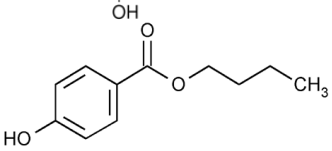
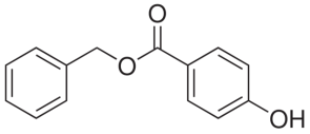
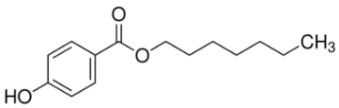
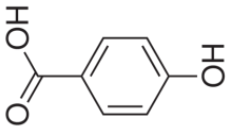
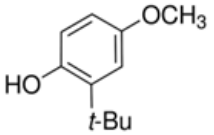
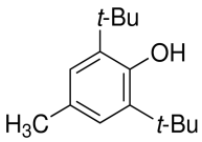
The expansion of human activities in modern society has resulted in extensive demands for a wide range of organic chemicals. Up to 2016, more than 106 million chemicals have been registered in the Chemical Abstracts Service (CAS, http://www.cas.org/) database with ca. 150 000 chemicals updated daily. Most of them are organic chemicals. These organic chemicals are manufactured for the purposes to improve the quality of life of people and to promote the development of society. They are used together with the products which contain them and are subsequently released into the environment. These organic chemicals include active pharmaceutical ingredients, personal care product ingredients, pesticides, hormones, industrial ingredients and contaminants and by-products etc. They are collectively termed emerging organic contaminants (EOCs) (Petrie *et al*., 2015) or trace organic chemicals (TOrCs) (Anumol and Snyder, 2015). Many of these chemicals have anthropogenic sources and have been produced in large quantities around the world. Thus, they are ubiquitously detectable in ecosystems in urban (Li *et al*., 2016; Wang *et al*., 2015a; Wang *et al*., 2015b), rural (Wang *et al*., 2015a; Wu *et al*., 2014) and remote areas (Sanch ś *et al*., 2015).

1.1.2 EOCs studies in this thesis

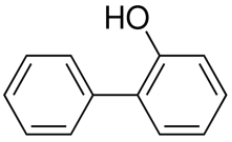
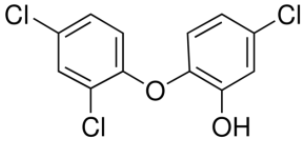
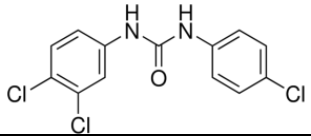
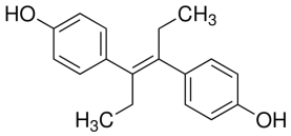
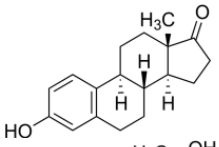
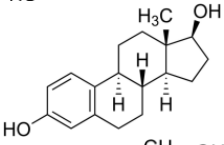
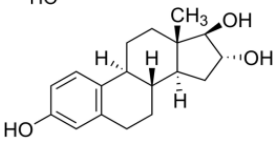
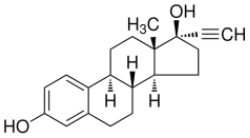
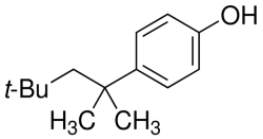
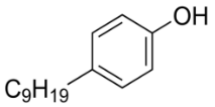
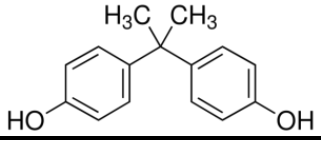
Household consumers use a wide range of home and personal care products and pharmaceuticals in their daily life, which contain a broad range of EOCs, including preservatives, antioxidants, disinfectants, oestrogens and surfactants (e.g. alkyl-phenols) etc. The selection of the EOCs in this thesis (**Table 1**) was based on the priorities of physical-chemical properties and usage of chemicals in China listed in the literature (Gouin *et al*., 2012) and their potential applicability for sampling by the technique of diffusive gradients in thin-

films (DGT). The chemicals in the list were firstly screened for their physical-chemical properties (logKow < 6 and water solubility > 0.5 mg L^{-1}) and then selected for the estimated usage/ emission in China and possible environmental concern (such as oestrogen, alkyl-phenol and BPA). At the same time, the target chemicals should cover the wide range of chemicals for daily use.

Table 1: Information of EOCs studies in this thesis[1].

Group	Chemical, abbreviation and CAS No.	Molecular formular	Molecular weight	Water solubility (mg L^{-1})[a]	pK_a[a,b]	Estimated emission (KT)[c]	LogK_{OW}[a,d]	Structure
Preservative	Methylparaben MEP 99-76-3	$C_8H_8O_3$	152.15	2500	8.31	1.00	2	
	Ethylparaben ETP 120-47-8	$C_9H_{10}O_3$	166.17	885	8.50	0.50	2.49	
	Propylparaben PRP 94-13-3	$C_{10}H_{12}O_3$	180.2	500	8.23	1.00	2.98	
	Butylparaben BUP 94-26-8	$C_{11}H_{14}O_3$	194.23	207	8.50	0.14	3.47	
	Benzylparaben BEP 94-18-8	$C_{14}H_{12}O_3$	228.25	23.419	8.49	-[e]	3.70	
	Heptyl paraben HEP 1085-12-7	$C_{14}H_{20}O_3$	236.31	8.022	8.50	-	4.94	
	4-Hydroxybenzoic acid PHBA 99-96-7	$C_7H_6O_3$	138.12	5000	4.38 9.67	-	1.39	
Antioxidant	Butylated hydroxyanisole BHA 25013-16-5	$C_{11}H_{16}O_2$	180.24	212.8	10.55	-	3.5	
	Butylated hydroxytoluene BHT 128-37-0	$C_{15}H_{24}O$	220.35	0.6	11.60	0.57	5.03	

[1] This table is continued onto the next page.

Group	Chemical, abbreviation and CAS No.	Molecular formular	Molecular weight	Water solubility (mg L^{-1})[a]	pK_a[a,b]	Estimated emission (KT)[c]	LogK_{OW}[a,d]	Structure
Disinfectant	Ortho-phenylphenol OPP 90-43-7	$C_{12}H_{10}O$	170.21	700	9.65	292.58	3.28	
	Triclosan TCS 3380-34-5	$C_{12}H_7Cl_3O_2$	289.55	10	7.68	1.72	4.66	
	Triclocarban TCC 101-20-2	$C_{13}H_9Cl_3N_2O$	315.59	0.65	11.42	-	4.90	
Oestrogen	Diethylstilbestrol DES 56-53-1	$C_{18}H_{20}O_2$	268.36	12	9.13 9.75	-	5.64	
	Estrone E1 53-16-7	$C_{18}H_{22}O_2$	270.37	30	10.33	-	3.43	
	β-Estradiol E2 50-28-2	$C_{18}H_{24}O_2$	272.39	3.9	10.33	-	3.94	
	Estriol E3 50-27-1	$C_{18}H_{24}O_3$	288.39	440.8	10.33 13.62	-	2.81	
	17*α*-Ethinylestradiol EE2 57-63-6	$C_{20}H_{24}O_2$	296.41	11.3	10.33	-	4.12	
Alkyl-phenol	4-*tert*-Octylphenol 4-*t*-OP 140-66-9	$C_{14}H_{22}O$	206.33	4.82	10.23	-	5.28	
	Nonylphenol NP 84852-15-3	$C_{15}H_{24}O$	220.36	7.62	10.30	-	5.77	
Bisphenol	Bisphenol-A BPA 80-05-7	$C_{15}H_{16}O_2$	228.29	120	9.65 10.45	-	3.64	

a: the data were predicted by EPI Suite 4.1; b *K*a: acid dissociation constant; c: estimated from Gouin *et al.*, 2012; d Kow: octanol–water partition coefficient; e: not available.

Owing to the widespread application/existence of EOCs in our daily consumables products, including foodstuffs (Błędzka *et al*., 2014; Liao *et al*., 2013a; Liao *et al*., 2013c), pharmaceuticals and personal care products/cosmetics (Błędzka *et al*., 2014; Guo and Kannan, 2013), it is not unexpected that they would be detected in these products and human tissue or excreta (Barr *et al*., 2012; Meeker *et al*., 2013; Sandanger *et al*., 2011; Wang *et al*., 2015a; Wang *et al*., 2013b). The polar and non-volatile nature of these EOCs results in their distribution and transport after consumption/administration being primarily in the aquatic environment and possible accumulation in aquatic food chains (Boxall *et al*., 2012; Daughton and Ternes, 1999). As a result of their high production tonnages, widespread usage and continual discharge, many EOCs have become ubiquitously detectable and pseudo-persistent in the aquatic environment across the world (Boxall *et al*., 2012; Bu *et al*., 2013; Daughton and Ternes, 1999; Liu and Wong, 2013; Tijani *et al*., 2013). For example, these EOCs have been widely detected in environmental matrices, including wastewater (Li *et al*., 2015a; Petrie *et al*., 2015; Sun *et al*., 2016), surface water (Li *et al*., 2016; Wang *et al*., 2013a; Wang *et al*., 2015b), groundwater (Li *et al*., 2015b), soil (Liu and Wong, 2013), sediments (Liao *et al*., 2013b), sludge (Clarke and Smith, 2011; Liao *et al*., 2013b), air/dust (Wang *et al*., 2012b) and organism (Tanoue *et al*., 2015; Wu *et al*., 2010; Xue *et al*., 2015) etc.

1.1.3 Regulation, risk assessment and environmental quality standards for EOCs

Some regulatory frameworks for chemical assessment, such as REACH in Europe (Registration, Evaluation, Authorization, and Restriction of Chemicals (European Parliament and Council of the European Union, 2006)), TSCA in USA (Toxic Substances Control Act, (Congress US, 1976)) and *Measures on Environmental Managements of New Chemical Substances* and corresponding provisions in China (MEP of China, 2010), have been established for chemical regulation and management and for human and environmental protection. Adapted to these frameworks, some schemes were applied for chemical assessment,

such as PBT (Persistent Bioaccumulative and Toxicity) assessment, while relatively small groups of hazardous chemicals have been fully risk assessed. Many EOCs are not included or assessed by these schemes due to the lack of the knowledge on understanding of their environmental fate and behaviour, and of suitable sampling and analytical methods as well as the toxicology data. Therefore, suitable and adaptable schemes or (screening) tools for assessing chemicals are needed to aid with the development of effective the chemical regulation (Hendriks, 2013).

The large usage of EOCs in daily products and their widespread occurrence in the environment will result in exposure to these chemicals. There has been discussion about possible adverse effects on target or non-target organisms (Błędzka *et al*., 2014; Boxall *et al*., 2012; Daughton and Ternes, 1999; Thomaidi *et al*., 2015) such as emergence of antibacterial resistance (Zhu *et al*., 2013) endocrine disrupting effects (Silva *et al*., 2012) and toxicity (Brausch and Rand, 2011) etc. Guidelines for chemical risk assessment are issued based on the toxicology/eco-toxicology data and methodology development of chemical hazard assessment (Wang et al., 2012a). Some practical tools, especially modelling tools have been developed and employed to study chemical fate and transport (Mackay, 2001; Zhu *et al*., 2014), bioaccumulation (Czub and McLachlan, 2004), human/wildlife exposure (McKone and Enoch, 2002) and for final risk assessment (Arnot *et al*., 2006; Gouin *et al*., 2012). Models used for risk assessment include the European Union System for the Evaluation of Substance (EUSES (Vermeire *et al*., 1997)), ECETOC Targeted Risk Assessment (TRA, http://www.ecetoc.org/tools/targeted-risk-assessment-tra/), Risk Assessment, IDentification, And Ranking (RAIDAR (Arnot *et al*., 2006)), ACC-HUMAN (Czub and McLachlan, 2004) and CalTOX (McKone and Enoch, 2002) models, etc. Many studies on developing risk assessment approaches have focused on conventional priority chemicals, such as persistent organic pollutants (POPs), because of the high level of understanding of their fate and behaviour along with available modelling tools. However, to the best of my knowledge, the

risk assessment for EOCs is relatively difficult owing to the poor-understanding of their environmental fate and behaviour, and the lack of suitable sampling and analytical methods for studying their fate and behaviour. Thus, there is a need to study the behaviour and fate of these EOCs under real conditions since they are emitted into the environment.

Environmental quality standards (EQSs) were set up to limit the level of the chemicals in the environment to maintain ecosystem function and protect the human health. However, they focused on conventional inorganic and selected organic pollutants (or priority pollutants) (Petrie *et al*., 2015). Few EOCs have been listed in as priority pollutants and have associated with EQSs due to the lack of supporting evidence of their harm to ecosystem and human health. For example, EOCs have not been listed and restricted by the Environmental Quality Standards for Surface Water developed in China (MEP of China, 2002). The EU-Water Framework Directive has just begun to include threshold levels for some EOCs (such as NP and OP were added as the priority substances in the EQS, and E2 and EE2 were added as the priority substances in the field of water policy) in the newest version (European Commission, 2012).

Providing data to evaluate potential risks of EOCs to ecosystems and human health to support the development of EQSs is extremely important. For example, it is necessary to know the status of their occurrence to offer supporting information on the study of their fate and behaviour in the environment. The fate and behaviour of EOCs in the real environment may be different from theoretical predictions. Thus, it is necessary to study the behaviour and fate of these EOCs under real conditions since they are emitted into WWTPs and into the environment.

1.2 Wastewater

With the continuous growth of the world population, the demand and consumption of the water resources are increasing, along with the associated wastewater discharge. The water

industry is facing the challenge to sustainably provide the clean water sources and efficiently treat the wastewater all over the world. Wastewater contains large amounts of contaminants which include suspended solids, biodegradable organics, pathogens and parasites, nutrients, priority pollutants, refractory organics, heavy metals, dissolved inorganics and emerging contaminants etc. (Bitton, 2005). Wastewater has to be treated before it can be discharged into the receiving water in order to minimise negative effects on the environment. In this thesis, the focus is primarily on the domestic wastewater, thus the wastewater refers to domestic wastewater unless stated specifically.

1.2.1 Wastewater and wastewater treatment in China

With the rapid development of industrialisation and urbanisation, the consumption of the water resources is increasing significantly in China leading to significant expansion in the wastewater treatment industry over the last two decades. According to data (**Figure 1**) from the MEP of China and MOHURD of China (Ministry of Environment Protection and Ministry of Housing and Urban-Rural Development of People's Republic of China), the volume of industrial wastewater discharge has not changed greatly over the past 2 decades. Indeed industrial wastewater discharge has been stable, or even decreased slightly since 2005, as restrictions on industrial discharge have been established in China. It can be estimated that industrial wastewater discharge will continue to decrease in the future. By contrast, the daily discharge of domestic wastewater in China has been continually increasing over the last 20 years, from ca. 41 million m^3 in 1995 to > 140 million m^3 in 2014. Domestic wastewater discharge is likely to have notable upward trends in the future, at ca. 2.5 billion tons/a as more infrastructure is being developed.

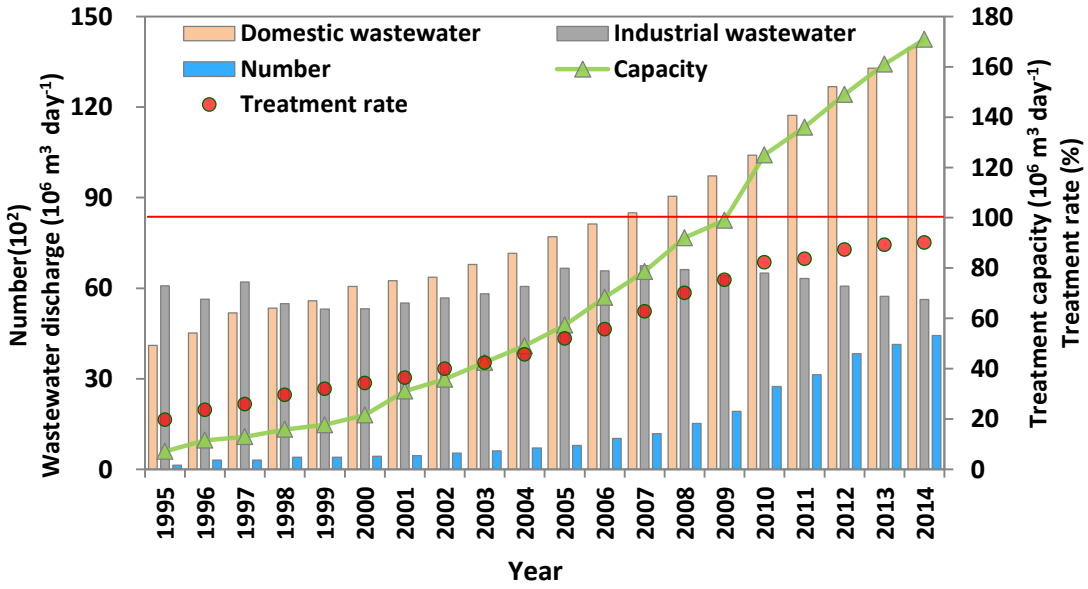


Figure 1: Daily average discharge of domestic and industrial wastewater, and wastewater treatment capacity (10^6 m^3 day^{-1}), number of WWTPs and treatment rate (%) in 1999-2014 of China, red line indicates the 100% of the treatment rate (Data from MEP of China).

To treat the large amounts of domestic wastewater and to adapt to the predicted increasing trends for wastewater discharge, a large number (ca. 4300) of WWTPs have been built over last 20 years, the total number of WWTPs has increased > 30 times since 1995. The total treatment capacity of WWTPs reached 171 million m^3 d^{-1} in 2014, which is ca. 23 times larger than in 1995. The wastewater treatment rate in urban area of China was improved with the increased number of WWTPs, and reached ca. 90% at the end of 2013, more than 3 times than in 1995. It can be projected that the number of WWTPs, the treatment capacity, and the treatment rate will keep on increasing because of the continuous growing of production of domestic wastewater across China.

Physical processes as well as chemical and biological processes drive the treatment of wastewater (Bitton, 2005). Treatments based on physical processes include screening, sedimentation, filtration, or flotation, whilst chemical treatment methods include disinfection, adsorption, or precipitation. The biological unit processes include the microbial reactions, which are responsible for organic matter degradation and removal of nutrients (N and P)

(Bitton, 2005). The combined processes including both chemical and biological ones are the main processes for wastewater treatment. The typical processes in a WWTP are shown below in **Figure 2**.

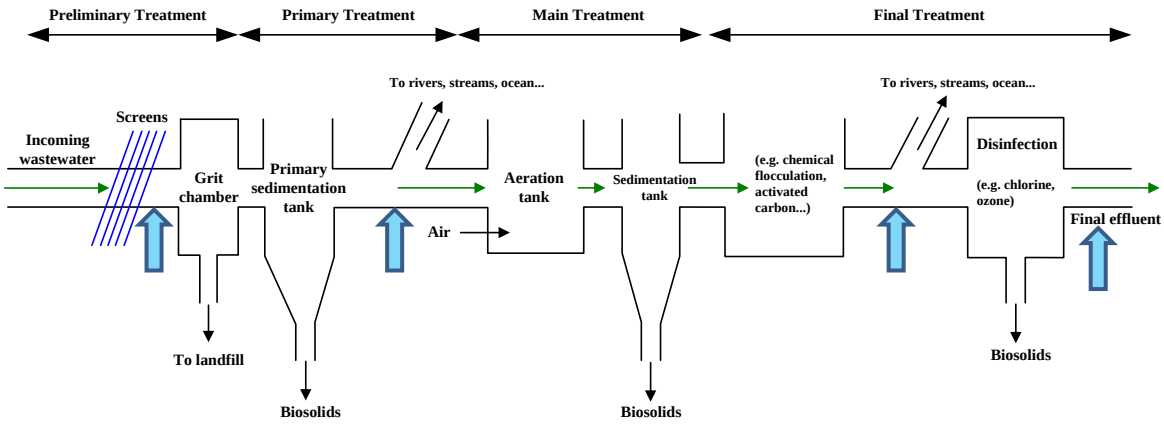


Figure 2: Processes of typical WWTPs and sampling sites.

Figure 3 shows the percentage of each main domestic wastewater treatment technology utilised by WWTPs in China (data from MEP of China in 2014). Activated sludge (AS) based techniques are the most widely-used main (secondary) processes in China accounting for 86 % in all the WWTPs, which includes oxidation ditch (OD) process (26%), anaerobic/anoxic/oxic (A2/O) process (25%), sequencing batch reactor (SBR) process (20%) and anaerobic/oxic (A/O) process (15%). The biological aeration filter (BAF) process, which belonged to another important process-the biofilm-process, was equipped for 9% of the WWTPs. Only 5% of WWTPs employed other techniques/processes.

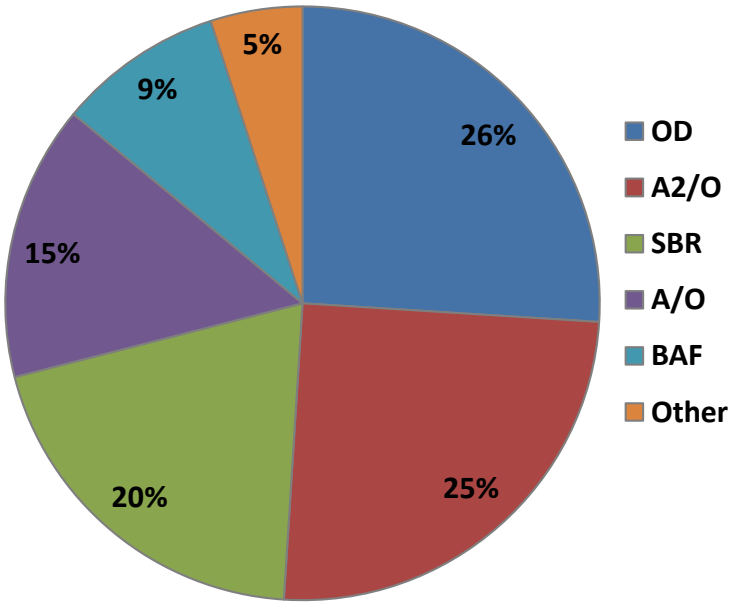


Figure 3: Percentage of main wastewater treatment technology in China.

1.2.2 Fate of EOCs during wastewater treatment

Conventional WWTPs are normally designed to eliminate solids, suspended particulates, nutrients, and dissolved biodegradable organic matter, but not specifically for the removal of emerging contaminants (Xu *et al*., 2012). After consumption, EOCs are not thought to be completely metabolized or transformed by organisms, with the remaining EOCs being excreted or washed 'down the drain' and directed to the sewage system. WWTPs are considered to be significant sources and the major routes of EOCs entering the environment (Błędzka *et al*., 2014; Kosma *et al*., 2014) because of the incomplete removal of these EOCs in the final effluent (Evgenidou *et al*., 2015a; Liu *et al*., 2015b; Petrie *et al*., 2015; Sun *et al*., 2016; Xu *et al*., 2012).

Some research has been conducted to study various aspects of the fate of EOCs in WWTPs, including their occurrence, spatial and temporal variation, physical-chemical processing, metabolism, mass-balances, loadings, and the removal of the EOCs in the WWTPs. Research has confirmed the widespread detection and occurrence of EOCs in the wastewater (from the raw influent to the final effluent) all around the world in both developed and developing

countries (Dai *et al*., 2014; Kim *et al*., 2009b; Kosma *et al*., 2014; Li *et al*., 2015a; Liu *et al*., 2015a; Racz and Goel, 2010). The concentrations of the EOCs may vary in the WWTPs located in different regions with different patterns, because of the different application/supply of the EOCs and economic variations in different regions, such as urban areas and sub-urban areas (Baker and Kasprzyk-Hordern, 2013; Chen *et al*., 2015; Sun *et al*., 2016). Some researchers have studied the intra-day, inter-day and seasonal variability of EOCs and showed that resident habits and activities over different periods (within day and between day) could result in the variability of EOCs (Harman *et al*., 2011; Kosma *et al*., 2014; Papageorgiou *et al*., 2016; Sun *et al*., 2016; Yu *et al*., 2013). The physical-chemical and biological processes are the key processes controlling the fate of EOCs in WWTPs, for example, the sorption of EOCs from aqueous phases onto sludge could reduce concentrations of the EOCs in water contributing to EOC removal (Clarke and Smith, 2011; Evgenidou *et al*., 2015b; Silva *et al*., 2012; Wang and Kannan, 2016; Xu *et al*., 2012), photo-degradation could also be a useful process to eliminate EOCs in the wastewater, though it may be not so important (Kim *et al*., 2009a; Silva *et al*., 2012; Sui *et al*., 2010). Biological process (microbial reactions) pose the most important process to transform and reduce EOCs in the wastewater (Liu *et al*., 2015b; Onesios *et al*., 2009; Petrie *et al*., 2015; Silva *et al*., 2012; Xu *et al*., 2012), although conventional processes may not be so effective for removal, and could even produce EOCs by metabolism resulting in higher concentrations in the effluents (Chen *et al*., 2015; Jelic *et al*., 2011; Onesios *et al*., 2009). Loading and mass-balance studies have also been conducted to assess the input and fate of EOCs throughout the treatment process (Liu *et al*., 2012; Papageorgiou *et al*., 2016; Sun *et al*., 2016; Wang and Kannan, 2016). Removal of EOCs during treatment is, hence, a very important factor in wastewater treatment (Chen *et al*., 2015; Evgenidou *et al*., 2015b; Kosma *et al*., 2014; Li *et al*., 2015a; Onesios *et al*., 2009; Papageorgiou *et al*., 2016; Sun *et al*., 2016; Xu *et al*., 2012). Removal efficiencies may be affected by many factors, such as physical-chemical properties of EOCs, physical-chemical

and biological processes, the type of the treatment process etc. Predictive models have been developed to assist with the development of an understanding of the fate and behaviour of EOCs in WWTPs, such as the fugacity model and SimpleTreat model, etc. (Blair *et al*., 2013; Bock *et al*., 2010; Fauser *et al*., 2003; Franco *et al*., 2013a, b; Seth *et al*., 2008).

Although many studies were conducted, nearly all the field data/results from these available studies are obtained from the conventional sampling method, the drawbacks and the uncertainties of the conventional sampling approach (Ort *et al*., 2010a; Ort *et al*., 2010b), such as grab sampling, due to the lack of the representative sampler, this would result in the unconfident results and/or incomplete conclusions for these studies. Therefore, there is a necessity to develop adaptable sampling approaches beyond the conventional sampling methods, to provide reliable and complementary field data for studying the fate and behaviour of EOCs in WWTPs and/or evaluating/validating the accuracy of the modelling. Recent progress in the development of passive sampling approach could be a good alternative to fulfil the need.

1.3 Passive Sampling

Passive sampling can be defined as any passive technique based on the free flow of analyte molecules from a sampled medium to a receiving phase as a result of a difference in chemical potential of the analyte between the phases (Górecki and Namieśnik, 2002; Vrana *et al*., 2005). The principle of passive sampling has been widely applied for air, water, soil/sediments monitoring (Górecki and Namieśnik, 2002; Seethapathy *et al*., 2008). This study focuses on the passive water sampling (PWS).

The *passive* in the PWS contrasts to *active*, showing the sampling process is driven without any energy sources but the difference in chemical potential (Vrana *et al*., 2005). Compared with the conventional sampling methods, such as grab sampling and auto-sampling, passive sampling offers a number of distinct advantages. For example, passive samplers provide an *in*

situ technique which accumulates the freely dissolved fraction of the target analytes without affecting the bulk solution, providing either equilibrium or time-weight average (TWA) concentrations (Mills *et al*., 2014; Morin *et al*., 2012). *In situ* pre-concentration by passive sampling can provide increased sensitivity (Morin *et al*., 2012) and reduce/eliminate the matrix interferences and solvent consumption (Seethapathy *et al*., 2008). It can minimise sample contamination (it is pre-selective), decomposition/degradation or loss/change in post-sampling transport and storage (Morin *et al*., 2012). It can also provide an economical and effective solution to contaminant sampling because of its simple design, operation and treatment (Chen *et al*., 2013). Therefore, passive water sampling has seen a remarkable rise in popularity for monitoring programmes in recent years (Mi ège *et al*., 2015; Mills *et al*., 2014; Vrana *et al*., 2016).

1.3.1 Passive water sampling

The first passive water sampling (PWS) device was developed in the 1970s for monitoring inorganic chemicals in natural water (Beneš and Steinnes, 1974). When the sampler is exposed to the sample matrix, the uptake of the analyte into the sampler follows the pattern shown in **Figure 4**, which can be described by a first-order, one compartment model (Mayer *et al*., 2003; Vrana *et al*., 2005):

$$C_s(t) = C_W \frac{k_1}{k_2}(1 - e^{-k_2 t}) \quad \textbf{(1)}$$

where $C_S(t)$ is the analyte concentration in the receiving phase of the sampler at the exposure time t, C_W the analyte concentration in the aqueous environment, and k_1 and k_2 are the uptake and offload rate constants, respectively. k_1/k_2 is the phase-water partition coefficient (K). According to this model, the uptake of analyte occurs until the chemical potential of the analyte in receiving phase is equal to it in the sample matrix. Three uptake regimes, kinetic, pseudo-linear or equilibrium can be observed when a passive sampler is deployed in the field under different conditions. Two main passive samplers are distinguished, based on the

operation regime: equilibrium passive sampler and kinetic passive sampler, which could provide equilibrium or TWA concentration of the analyte of concern.

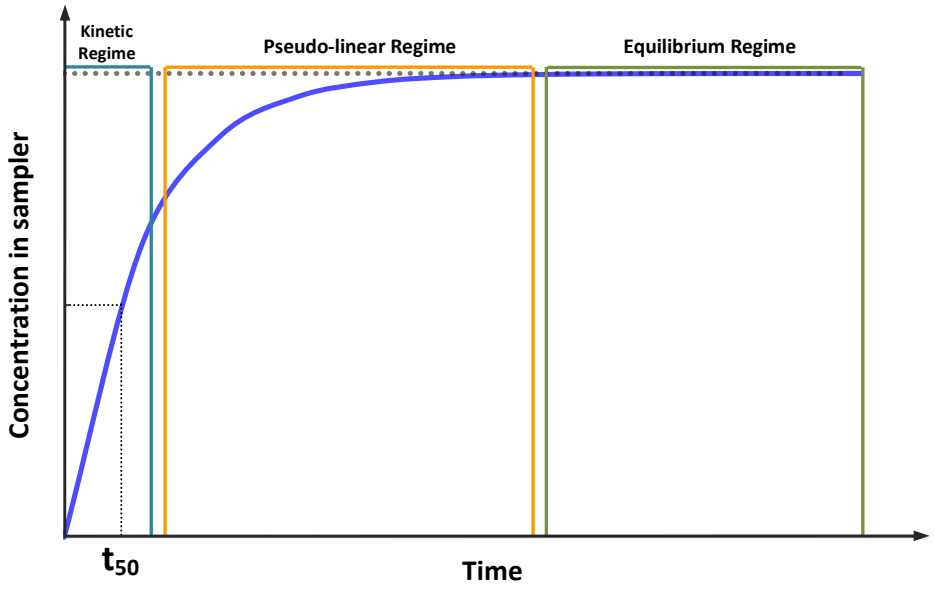


Figure 4: Analyte mass uptake in the passive sampler.

For equilibrium passive sampling, thermodynamic equilibrium is established between the water and receiving phases after a sufficiently long time of exposure. The Equation (1) can be rewritten under this condition:

$$C_s = C_W \frac{k_1}{k_2} = C_W K \qquad \textbf{(2)}$$

For kinetic passive sampling, the sampler works in the linear uptake regime: the analyte mass accumulated into the receiving phase is linearly proportional to the difference of chemical potential between the water and receiving phases, and desorption can be negligible. Thus, the Equation (1) can be reduced to:

$$C_s(t) = C_W k_1 t \qquad \textbf{(3)}$$

Equation (3) can be also rearranged to an equivalent relationship:

$$M_s(t) = C_W R_S t \quad \textbf{(4)}$$

where $M_S(t)$ is the analyte mass accumulated in the receiving phase of the sampler after exposure time t, where R_S is the proportionality constant/sampling rate for the analyte in the water. The TWA C_W can be calculated based on a known sampling rate (R_S), exposure time (t) and the amount ($M_S(t)$) of analyte trapped by the receiving phase.

1.3.2 Passive water sampling for organic chemicals

Since the first PWS device was developed in 1970s (Beneš and Steinnes, 1974), it was not until 1987 that a PWS was introduced for organic chemicals (Soedergren, 1987). Since then passive water sampling methods for organics have become popular and made enormous advancements over last 3 decades (Górecki and Namieśnik, 2002; Mi ège *et al*., 2015; Mills *et al*., 2014; Mills *et al*., 2007; Seethapathy *et al*., 2008; Stuer-Lauridsen, 2005; Vrana *et al*., 2005).

A number of PWS devices have been developed and available for sampling of various organic chemicals from water. Some previous publications (Booij *et al*., 2016; Greenwood *et al*., 2007; Mi ège *et al*., 2015; Seethapathy *et al*., 2008; Stuer-Lauridsen, 2005; Vrana *et al*., 2005; Vrana *et al*., 2016) have summarized the general information for these samplers including name, construction, operation regime, target chemicals, receiving phase etc. Semipermeable membrane devices (SPMDs, 1990), polar organic chemical integrative sampler (POCIS, 1999) and Chemcatcher (organic version, 2000) are among the most widely-used and commercialised PWS for organic chemicals. SPMDs described by Huckins *et al*. (Huckins *et al*., 1990) are designed for monitoring hydrophobic or non-polar organic chemicals (HOCs) in waters, such as POPs (Booij *et al*., 2016; Miège *et al*., 2015). POCIS and Chemcatcher (organic version) are developed for polar or hydrophilic organic chemicals (POCs) or EOCs monitoring in aquatic environment (Miège *et al*., 2015). Many chemicals can accumulate in the PWS including pharmaceuticals, personal care products, polar pesticides, acid herbicides,

perfluorinated chemicals, alkyl-phenols etc., which have been described in the literature (Harman *et al*., 2012; Kaserzon *et al*., 2012; Miege *et al*., 2012; Miège *et al*., 2015; Mills *et al*., 2014; Morin *et al*., 2012; Moschet *et al*., 2015). These studies demonstrate the potential of PWS devices.

For most passive samplers, including SPMDs, POCIS and Chemcatcher, *in situ* and/or laboratory calibration data are required before they can be applied for field application (Harman *et al*., 2012; Mills *et al*., 2014), where calibration is dependent on the hydrodynamic conditions such as water flow and some other environmental parameters (Charlestra *et al*., 2012; Li *et al*., 2010). Such factors can result in considerable measurement uncertainty (Harman *et al*., 2012; Mills *et al*., 2014). Therefore, performance reference compounds (PRCs) are used to provide calibration data to assess the difference between the *in situ* sampling rates (R_S) and laboratory derived values (Belles *et al*., 2014; Harman *et al*., 2012; Vallejo *et al*., 2013). This can be problematic for polar chemicals. Furthermore, the performance of the samplers when they are deployed, can be affected under varying environmental conditions, such as water flow and turbulence, temperature, pH, salinity/ ionic strength (IS), dissolved organic matter (DOM) and fouling/biofouling (Harman *et al*., 2012; Li *et al*., 2011; Li *et al*., 2010; MacLeod *et al*., 2007; Togola and Budzinski, 2007). Due to these barriers, more advanced passive water sampling devices are needed for EOCs monitoring under changing conditions of aquatic environment to provide reliable data.

1.3.3 DGT sampling for organic chemicals

The passive sampling technique of diffusive gradients in the thin-films (DGT) developed by Davison and Zhang in 1994 (Davison and Zhang, 1994), has been demonstrated to be able to provide quantitative *in situ* measurements of trace chemicals in aqueous systems (Zhang and Davison, 1995). Unlike other passive samplers, *in-situ* calibrations are not necessary for DGT, as the transport of the analyte is solely controlled by its molecular diffusion (Davison and

Zhang, 1994; Zhang and Davison, 1995, 1999). So it is less affected by environmental conditions as mentioned in above section, making it is able to provide reliable data under varying conditions.

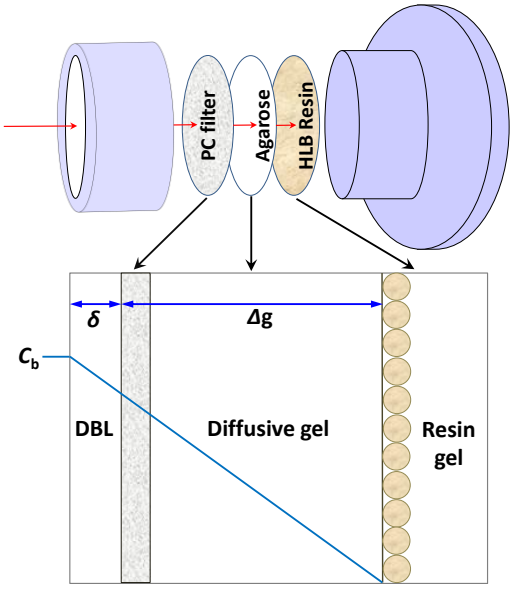


Figure 5: Principle and structure of DGT sampler used in this thesis.

A typical DGT device contains a backing cylinder and a front cap with 2 cm diameter window. A resin gel layer followed by a diffusive gel and protective filter are placed together and held securely between the top of the cylinder and the back of cap (**Figure 5**). The principle of the DGT sampler, based on Fick's first law of diffusion, has been reported previously (Davison and Zhang, 2012; Zhang and Davison, 1995). The DGT measurement, C_{DGT}, provides the TWA concentrations of organics in the solution, which is expressed using the Equation (5) (Zhang and Davison, 1995):

$$C_{DGT} = \frac{M(\Delta g + \delta)}{D_e A t} \quad \textbf{(5)}$$

where M is the measured mass of target chemical accumulated in the binding gel, Δg is the thickness of the diffusive layer, δ is the thickness of diffusive boundary layer (DBL), D_e is the diffusion coefficient of target chemical and A is the exposure window area of the cap. Δg is much thicker than the typical thickness of DBL under most conditions so that the influence of

the DBL becomes negligible, making the DGT measurement fairly insensitive to hydrodynamic conditions (Davison and Zhang, 2012; Zhang and Davison, 1995).

Table 2: Recent DGT research for organic compounds in waters.

Target compounds	Resin	Diffusive layer	Filter	Capacity (μg per gel)	Applicable pH	Applicable IS, M	Ref
Antibiotics	XAD18	Agarose	PES	360 for SMX	6.2-9	0.001-0.1	(Chen *et al*., 2012; Chen *et al*., 2013)
Phenol and 4-CP	MIP	Nylon membrane	-	11.0 (phenol) and 31.5 (4-CP) mg/g	3-7	0.0001-0.1	(Dong *et al*., 2014a; Dong *et al*., 2014b)
Bisphenols	Activated charcoal	Agarose	hydrophilic PTFE	140 (BPB), 190 (BPF) and 192 (BPA)	4.98-7.73	0.001-0.5	(Zheng *et al*., 2015)
PMG, AMPA	TiO_2	Polyarylamide	PES	2.57 (PMG) and 2.34 (AMPA)	5-8.5	UPW	(Fauvelle *et al*., 2015)

Theoretically, DGT can be applicable to any inorganic or organic diffusing species although almost all the results are focused on the inorganic measurement (Davison and Zhang, 2012; Zhang and Davison, 2015) and few studies on organic measurements have been reported. Recently, several attempts have been made on the DGT measurements of organic substances. For example, Chen *et al*. (Chen *et al*., 2012; Chen *et al*., 2013) successfully extended the application of DGT using XAD18 as the binding resin to measure 37 antibiotics in waters, Dong *et al*. (Dong *et al*., 2014a; Dong *et al*., 2014b) subsequently used this sampler with molecularly imprinted polymers (MIP) as the binding agents to sample phenol and 4-chlorophenol (4-CP) in water, Zheng *et al*. (Zheng *et al*., 2015) have also successfully applied DGT to 3 bisphenols (BPs) using activated charcoal as the binding layer and more recently, Fauvelle *et al.* (Fauvelle *et al*., 2015) applied titanium dioxide (TiO_2) as binding phase for DGT to detect glyphosate (PMG) and aminomethyl phosphonic acid (AMPA) in the aquatic environment. **Table 2** summarises some recent DGT research on organic compounds. These studies demonstrated that the DGT technique is potentially capable for monitoring organic chemicals, especially for EOCs in aquatic environment, by selecting suitable materials/ resins.

1.4 Objective of This Thesis

The occurrence and removal of EOCs through the sewage treatment process has been studied widely in developed countries, but not in China where urbanisation is increasing rapidly and provision of treatment facilities varies greatly. Meanwhile, China represents a significant and growing market for many of these chemicals. Thus, it is not surprising that a large number of organic chemicals would enter the wastewater treatment process and there is concern about the removal efficiencies of the treatment processes. Therefore, the overall objective of this thesis is to study the fate of EOCs in Chinese wastewater treatment plants utilising DGT passive sampling techniques, and provide an alternative tool for the environmental monitoring of these EOCs and for the further assessment of their potential risk. More specifically to:

1) Develop DGT techniques for *in situ* measurements of selected EOCs in waters using hydrophilic-lipophilic-balanced (HLB) resins as binding agents and 11 typical EOCs as model chemicals (**Paper I**);

2) Evaluate the performance of three different types of resins (HLB, XAD18 and SXLA (Strata-XL-A)) for EOCs when developing the DGT technique and its implication for DGT development in the future (**Paper II**);

3) Develop and validate the analytical method for 20 selected EOCs in the river water and wastewater, including pre-treatment methods and instrumental determination by two different systems of mass spectrometry (**Paper III**);

4) Evaluate and validate the DGT passive sampling techniques for EOCs in the influent and effluent of a UK WWTP by comparison with conventional sampling approached such as grab and auto-sampling (**Paper IV**);

5) Study the occurrence of EOCs and their removal in 10 Chinese WWTPs located in Dalian and Wuhan utilising the developed DGT technique and evaluate the effects of different treatment facilities on the removal efficiency (**Paper V**).

2. Methodology

A brief overview of methods applied in this thesis, including 1) the laboratory tests for DGT development for EOCs in waters and for optimisation of the analytical methods, 2) field campaigns for optimisation of pre-treatment and instrumental methods, DGT validation in UK and field application of DGT in 10 Chinese WWTPs, 3) pre-treatment, instrumental analysis and procedures of quality assurance/quality control of DGT samples and water samples for both laboratory tests and field campaigns, and 4) principle and equations for data acquisition and calculation, and data statistics, are given below. Detailed description of the methodology can be found in individual papers.

2.1 Laboratory Tests

Controlled laboratory tests were conducted for developing the DGT technique for EOCs in waters (**Paper I**, **II** and **IV**) and the optimisation of the analytical methods (**Paper I** and **III**) for water samples. The materials used for making DGT devices, including the plastic DGT holders (piston and cap), two types of diffusive gels and five types of membrane filters, were assessed for possible adsorption of 11 test chemicals (**Paper I**). The test or model chemicals for DGT development are methylparaben (MEP), propylparaben (PRP), isopropylparaben (IPRP), bisphenol-A (BPA), estrone (E1), β-estradiol (E2), estriol (E3), 17α-ethinylestradiol (EE2), butylated hydroxyanisole (BHA), ortho-phenylphenol (OPP) and triclosan (TCS). Diffusion coefficients (D_e) of EOCs were measured by a two-compartment diffusion cell connected by a circular window (1.5 cm diameter) with a 0.8 mm diffusive gel (agarose gel) according to a published procedure (Zhang and Davison, 1999) (**Paper I** and **IV**), these D_e data were then applied for TWA concentration calculation in later studies (**Paper I**, **II**, **IV** and **V**). The validation of the DGT principle was confirmed by linear accumulation of test chemicals with time up to 5 days (**Paper I** and **II**) and with the inverse proportion to thicknesses of the diffusion layer (**Paper I**). The DGT performance for 11 test EOCs under

different simulated environmental conditions with changing pH (3.5-9.5), IS (0.001-0.5 M) and DOM contents (0-20 mg L^{-1}), were tested for DGT with HLB resin (**Paper I**) and compared with other DGT equipped with XAD18 and SXLA resins (**Paper II**) by deploying DGT devices into chemical spiked solutions with a stirring speed of 350 revolutions per minute (rpm) by a magnetic stir bar for ca. 20 hours (h). DGT devices with different resin gels (HLB, XAD18 and SXLA) were exposed into solutions of various concentrations of 11 test chemicals and tested for uptake capacity (**Paper I** and **II**), uptake kinetics of 11 test chemicals by HLB, XAD18 and SXLA binding gels was investigated by immersing gel discs in solutions for different periods of up to 24 h (**Paper I** and **II**). The effect of water turbulence was investigated by deploying DGT with different water flow rates simulated by a magnetic stir bar with various stirring speeds (**Paper I**).

The analytical method (**Paper I** and **III**) was optimised for water samples, including the solid-phase extraction (SPE) pre-treatment and instrumental method validation. A minor optimisation of an SPE method based on previous studies (Gonzalez-Marino et al., 2009; Yu et al., 2011) was applied to the analysis of water samples in **Paper I**. Spiked river water samples were extracted under different pH conditions (pH 2.5 and 7) with different SPE cartridges (Oasis-HLB from Waters, Supel-Select HLB from Sigma-Aldrich and Strata-X from Phenomenex) and then eluted by various organic solvents (MeOH, ACN, EA and their mixture) to systematically optimise the best SPE condition for 20 EOCs in waters (**Paper III**). This optimized SPE method was used in later studies in this thesis (**Paper II, IV** and **V**). The SPE recoveries, overall recoveries and matrix effects were tested using river water and wastewater to evaluate the performance of both SPE pre-treatment and instrumental analysis (**Paper III**). The accuracy of instrumental method evaluated with the percentage of deviation of results for samples with known (added) amounts of analytes and precision was estimated by the intra-day and inter-day reproducibility using the relative standard deviation (RSD) of replicate measurements (**Paper III**).

2.2 Field Campaigns

Two main field campaigns were designed for DGT validation in the UK (**Paper I**, **II** and **IV**) and field application of DGT for EOC monitoring in 10 Chinese WWTPs located in Wuhan and Dalian (**Paper V**). A simple sampling study was also conducted to provide samples for optimisation of the pre-treatment as well as the environmental application when developing the analytical method for the EOCs in river water and wastewater (**Paper III**). The UK field campaign was undertaken at a WWTP with traditional activated sludge treatment process and service population of ca. 100 000 (**Paper I**, **II** and **IV**), DGT devices with HLB, XAD18 and SXLA resins were deployed for different periods up to 4 weeks under ca.30 cm water surface at both influent and effluent from the WWTP, DGT devices with XAD18 and SXLA resins were deployed for 2 weeks. DGT devices with HLB resin and different thicknesses of diffusion layer were also deployed for estimating the thickness of DBL in the influent and effluent (**Paper IV**). Active samples from auto-samplers (24-hour composite) and grab-samples were collected daily at the same sites. Only 14 day's DGT samples and part of the auto and grab-samples were used in **Paper I** and **II**. For the field campaign in China (**Paper V**), DGT devices with HLB resins were deployed in 10 WWTPs (located in Wuhan and Dalian, 5 in each city) for 1 week at four sites in each WWTP from raw influent to final influent (**Figure 2**). Grab samples were also collected from each site during DGT deployment and retrieval in China. The water temperature and pH was recorded during both field campaigns (**Paper I**, **II**, **IV** and **V**).

2.3 Analysis

2.3.1 Sample pre-treatment

Samples collected in this thesis include DGT samples (**Paper I**, **II**, **IV** and **V**) and water samples (**Paper I-V**). The pre-treatment included the ultrasonic extraction for the DGT

samples and the preparation or SPE extraction of water samples as well as their concentration and reconstitution.

The ultrasonic extraction procedure for DGT binding gels was optimised with extraction time, number of extractions and solvents (**Paper I** and **II**). All the DGT samples in this thesis (**Paper I**, **II**, **IV** and **V**) were extracted with the optimised procedures. The detailed procedures for optimised DGT extraction are fully described in **Paper I**. The same procedure was also applied for field DGT samples, but 100 ng of individual isotope-labelled internal standards (ISs) were added before extraction (**Paper I**, **II**, **IV** and **V**).

Water samples collected in the field were extracted by SPE. The SPE procedure in **Paper I** was undertaken according to published procedures (Gonzalez-Marino et al., 2009; Yu et al., 2011) with minor modification. Systematic optimisation of SPE extraction for pH, cartridge type and elution solvents was conducted for field water samples in **Paper III** and applied for studies in **Paper II**, **IV** and **V**. The detailed procedures for optimised SPE extraction are fully described in **Paper III**.

The extracts from DGT samples produced in the laboratory tests (**Paper I** and **II**) were then diluted with 50% Milli-Q (MQ) water before instrumental analysis. Water samples in the laboratory tests were collected directly from the container and prepared with water and methanol (50 %: 50 %) for instrumental analysis (**Paper I** and **II**). Field sample extracts (both DGT and water, **Paper I**-**V**) were then reduced to about 1 mL under a gentle flow of N_2, followed by syringe filtration (Whatman, PEFE, 0.22 μm) and placed in amber vials, stored at -20 ℃ awaiting liquid chromatography- mass spectrometer (LC-MS) analysis. Just prior to the LC-MS analysis, an aliquot of each water sample extract was dried under a gentle N_2 flow and reconstituted into 100 μL (50 μL for DGT samples) of water and methanol mixture (50 % : 50 %, v/v) with 5 mM mobile phase additive added.

2.3.2 Instrumental analysis

Four instruments were used for analysing the samples produced by the laboratory tests (**Paper I** and **II**) and field (**Paper I-V**), including a Thermo Finnigan high performance liquid chromatography coupled with a photodiode array detector (HPLC-DAD) for determining 11 test chemicals in the samples of lab test of **Paper I** and **II**, an Agilent 1100 HPLC system with Agilent 6100 single quadrupole mass spectrometer (HPLC-SQ-MS) equipped with an electrospray ionisation (ESI) source for analysing 11 test chemicals in field samples in **Paper I**, an Agilent 1100 HPLC system with a Quattro Micro triple-quadrupole mass spectrometer (Micromass, Manchester UK, HPLC-QqQ MS) for analytical method development of 20 EOCs in river water and wastewater (**Paper III**) and field sample analysis of 11 test chemicals in **Paper II** and of 20 EOCs in both DGT and wastewater samples in **Paper III-V**, and an ultrahigh performance liquid chromatography (Dionex, Ultimate 3000)-hybrid quadrupole-Orbitrap high resolution mass spectrometer system (UHPLC-Q-Orbitrap HRMS, Q-Exactive, Thermo Fisher Scientific, Germany) used for analytical method development of 20 EOCs in river water and wastewater by comparison with HPCL-QQQ-MS in **Paper III**. The operating conditions, including mobile phases and gradient programmes, columns and MS parameters, are fully described within the individual papers.

The identification of 11 target chemicals in samples from the laboratory tests was conducted by comparing the retention time and maximum ultraviolet (UV) absorbance of 260 nm or 280 nm of each chemical with standards for HPLC-DAD analysis, a six-point response calibration external standard method was established to quantify the target analyses in the laboratory tests (**Paper I** and **II**). The target chemicals in the field sampling were identified by the retention time and target ions/ ion transitions by comparison with the standards, and a response factor calibration curve for an internal standard method was established for quantification of the target chemicals (**Paper I-V**). The instrument detection limits (IDLs) for each instrument were

calculated based on the 3 times of signal-to-noise ratio (S/N >3) and the method detection limits (MDLs) were then calculated based on IDLs, which were showed in individual papers.

2.3.3 Quality assurance/quality control

The quality assurance/quality control (QA/QC) procedures were conducted for experiment preparation, sample collection, sample pre-treatment and analysis for both laboratory tests and field sampling in the thesis, which are fully described in individual papers.

All glassware used in the laboratory tests and field sampling campaigns was pre-cleaned and baked (450 ℃ for 4 h) before use. Other equipment/materials which came into direct contact with samples, such as plastic containers, DGT plastic holders and membrane filters, were cleaned with MeOH and MQ water before use. All the laboratory tests were undertaken in a cool, dark room and the water containers covered by aluminium foil to prevent possible photo-degradation of test chemicals during the deployment period, 0.02 % of NaN_3 was added into the solution to repress the microbial activities and bio-degradation. All the laboratory experiments and field sampling deployments of DGT were carried out at least in triplicate unless stated specifically, parallel bank and control studies were accompanied with laboratory test experiments. Field blank samples of DGT were prepared and analysed for field sampling.

For sample pre-treatment, blank and replicate samples were also pre-treated in each set of extractions for both DGT and water samples. Recoveries of DGT extraction and water sample SPE extraction for both river water and wastewater were tested by spiking target chemicals and ISs before the extraction. The matrix effects for the water samples were also assessed for water analysis by LC-MS. A set of calibration standards was run before analysis of each batch of samples. Solvent blank samples and QC standard samples were injected daily to check for interference and cross contamination, and the instrument performance.

2.4 Data Calculation and Statistics

2.4.1 Calculation of TWA concentration

In order to calculate the TWA concentrations of EOCs measured by the DGT samplers, it is necessary to know the diffusion coefficients (D_e) of target EOCs at different temperature in the water. The D_e for EOCs at 25 ℃, D_{25}, were measured and listed in **Paper I** and **IV**. The D_e at other temperatures (T), D_T, could be calculated by Equation (6) (Zhang and Davison, 1995). The D_e for 11 test chemicals at 15 and 20 ℃ were also measured to evaluate the accuracy of the measurement at 25 ℃ (**Paper I**).

$$\log D_T = \frac{1.37023(T-25)+8.35\times10^{-4}(T-25)^2}{109+T} + \log\frac{D_{25}(273+T)}{298} \quad \textbf{(6)}$$

The DBL can affect the accuracy of DGT measurement. It exists between solid and liquid interfaces (membrane and solution for DGT) and cannot be eliminated thoroughly. However, the effect can be reduced by proper experimental design (Kingston et al., 2000) for example by using a relatively thick diffusive layer or under suitable hydrodynamic conditions (Zhang and Davison, 1995). Under most conditions, the effect of the DBL is thought to be negligible and so Equation (5) can be simplified to Equation (7):

$$C_{DGT} = \frac{M\Delta g}{D_e A t} \quad \textbf{(7)}$$

This equation was used to calculate TWA concentrations in **Paper I** and **V** with the exception for the experiment of assessing the effect of the DBL in **Paper I**, as well as the TWA concentrations for the laboratory test in **Paper II**.

Normally, the DBL varies with water flow rates and it is the same for all the analytes when the flow rate is constant. When the effect of the DBL needs to be accounted, the TWA concentrations can only be calculated by Equation (5). The thickness of the DBL could be estimated using Equation (8), which is rearranged from Equation (5), by simultaneously

deploying the DGT devices with different thicknesses of diffusion layer over the same time period. The reciprocal of accumulated masses of EOCs ($1/M$) is then plotted against the thickness of diffusive layer (Δg) and the δ could be calculated using the ratio of the intercept and the slope of the regression line.

$$\frac{1}{M} = \frac{\Delta g}{D_e C_{DGT} A t} + \frac{\delta}{D_e C_{DGT} A t} \quad \textbf{(8)}$$

Once the thickness of the DBL was estimated, the TWA concentration of EOCs could be calculated by Equation (5). It was used to calculate the TWA concentration in **Paper I** for the experiment of the effect of the DBL, in **Paper II** for the field DGT results and in **Paper IV**.

2.4.2 Data statistics

The statistical analysis was conducted by IBM *SPSS* Statistics software (Version 22), the significant differences were tested by analysis of variance (ANOVA) at 5 % significance level for the whole thesis.

3. Results and Discussion

A brief overview of the key findings in this thesis is given below. Detailed results and discussion can be found in the individual papers.

3.1 DGT Development for EOCs

Paper I and **IV** demonstrated the potential application of DGT principle for *in situ* measurement of several groups of EOCs in waters with HLB resin as novel binding agent. The laboratory tests (**Paper I**) and field validation (**Paper IV**) confirmed its applicability.

3.1.1 Validation of DGT principle for EOCs in the laboratory

The time and diffusion layer thickness dependence were used to confirm the validity of the DGT principle for the test chemicals in the laboratory (**Paper I**). DGT devices with HLB resin gels were deployed in water solutions spiked with 11 test chemicals for different time periods up to 5 days, and DGT samplers with different thicknesses of diffusion layer were simultaneously exposed into the solution for the same period.

The 5-day experiment showed that DGT can simultaneously and continuously accumulate the test chemicals and the accumulated test chemical amounts increased linearly (R^2 ranged from 0.9853 to 0.9995, $p < 0.001$) with the deployment time, which agreed well with the theoretical prediction, indicating DGT samplers with HLB resins can be used for measuring the selected test chemicals in solution directly and accurately. The accumulated amounts of the test chemical on the resin gels was found to be inversely proportional to the diffusion layer thickness and agreed well with the theoretical prediction. The results on both time and diffusion layer thickness dependence further confirm DGT theory and mechanism, and validate the direct use of DGT for simultaneous measurements of the 11 test chemicals in solution.

3.1.2 Uptake of EOCs in wastewater

The DGT devices with HLB resin were deployed in the influent and effluent streams in a UK WWTP for up to 28 days (**Paper IV**). Not all EOCs could be detected after 4 days' deployment in both influent and effluent, indicating 4 days' deployment was not enough to acquire reliable data. A 7-day deployment of DGT was sufficient for all detected EOCs in both influent and effluent as all detected EOCs could be found in 7-day's o-DGT samples. For the majority of EOCs detected by DGT (except BPA and TCC), the amounts continually accumulated from 7 days to 18 days, with a plateau being reached after this period. There would appear to be 3 possible reasons for a reduction in sampling rate or a decline in the mass retained on the resin gel - namely biofouling, degradation of compound held on the resin, or uptake and retention of co-existing/competing substances. Thus, 7-18 days' deployment of DGT devices will be effective for *in situ* measurement of most EOCs providing both enough low detection limits and continuous accumulation.

3.1.3 DGT compared with active sampling

Active sampling including auto and grab-sampling were undertaken to compare the results with the DGT sampling approach (**Paper IV**). For most detected EOCs in DGT, the concentrations were similar with the results from auto-sampling. For individual EOCs detected by the DGT, the TWA concentrations provided by DGT for different time durations also agreed well with the average concentrations delivered from auto-samples. Grab-sample results gave greater differences when comparing with DGT and auto-samples for the concentrations, variations and the patterns. The data suggested that the grab sampling method was not always representative of longer term variability, only a reflection of concentrations at the time of collection.

3.1.4 Effect of environmental conditions for DGT measurement

Some environmental factors such as pH, IS and DOM can affect the performance of DGT for *in situ* measurement. These effects were characterized (**Paper I**) under the laboratory conditions by exposing the DGT devices in the solution (spiked with test chemicals) with different pH, IS and DOM contents. HLB-DGT was found to be generally independent of solution pH (3.5-9.5) for the majority of test chemicals (except TCS), so it can be directly applied in most field conditions with wide range of pH values. No significant differences were observed for the majority of test chemicals when the IS concentration was 0.001-0.1 M, but significant reduction in C_{DGT}/C_b (> 10%) was observed when IS increased to 0.5 M, indicating HLB-DGT is suitable for use in freshwater but not in seawater unless the IS effect is further calibrated in the future. The ratios of C_{DGT}/C_b for most test chemicals are within the range of 0.9-1.1, except for TCS, when the DOM concentrations increase from 0 to 20 mg L^{-1}, showing that HLB-DGT performs well for the majority of test chemicals under different DOM concentration range and therefore it can be applied in the most aquatic environments.

When DGT devices are deployed under the real world conditions, some other factors, such as the (bio-)fouling and co-existing/ competition of other chemicals in the aquatic environment, especially in the wastewater, may have some influences on *in situ* measurements of DGT. The (bio-)degradation of the target chemicals during the deployment period could also affect the *in situ* measurement of DGT in the field. Field testing of DGT (**Paper IV**) in the UK WWTP indicated that the factors mentioned above could impact the performance in the field.

3.1.5 DBL effect on DGT measurement

The DBL could affect the accuracy of DGT *in situ* measurement for EOCs. The effect of DBL was studied in the laboratory (**Paper I**) under different water flow rates simulated by a magnetic stir bar with various stirring speeds and estimated *in situ* when validating the DGT techniques in the field (**Paper IV**).

Under the quiescent condition (stirring rate = 0 rpm), the C_{DGT} of test chemicals would be ca. 30 % underestimated due to the DBL effect. The DBL effect dramatically reduces with the water flow, and was found to be negligible compared to the diffusion layer when the stirring rate was ≥ 200 rpm. The stirring rate was set at 350 rpm for all the other experiments for the lab test (**Paper I** and **II**) to ensure the DBL was negligible.

To assess the *in situ* DBL thickness (δ) in the influent and effluent of WWTPs, DGT devices with various thicknesses of diffusive gel layer were deployed simultaneously in both influent and effluent (**Paper IV**). It was demonstrated that $1/M$ of EOCs accumulated by DGT was proportional to the thickness of the diffusive gel layer (Δg). The average DBL thickness in the influent and effluent was estimated to be 0.25 and 0.07 mm, respectively. The smaller DBL thickness in the effluent than in the influent was consistent with the observation in the field: more turbulent flow was in the final effluent. The TWA concentration measured by DGT (1 mm thick diffusion layer) will be ca. 20% and 6% underestimated in the influent and in the effluent, respectively, if the DBL effects were not considered. The results indicated that the effects of DBL should only be considered when DGT devices were deployed in waters with very slow flow rate or in the still water.

3.2 Binding Resin Selection of DGT Development for EOCs

Three types of resins (HLB, XAD18 and SXLA) were evaluated when developing DGT for EOCs based on the aspects of their sorption behaviour with EOCs and performance under a range of environmental conditions (**Paper II**).

3.2.1 Sorption of EOCs on different resins

The three types of resin gels were found to uptake the 11 test chemicals with comparable linear responses at low concentrations at both pH 6 and pH 8. Any differences in uptake appeared among the resin gels as well as between two pH systems after the linear phase and the uptake rate slowed although the resin gels could still continue to accumulate with

increasing solution concentrations. The Redlich-Peterson sorption isothermal model could better explain the sorption behaviour for the majority of EOCs than other sorption isothermal models such as, Langmuir and Freundlich according to the data fitting, indicating that the heterogeneous pores and surfaces of the resins could play an important role for sorption process for all these three resins.

Maximum sorption capacity (Q_{max}) of three different resins for individual chemicals (except for TCS) was estimated by the Langmuir model. The Q_{max} together with differences in chemical properties among the test chemicals can be used to understand the sorption behaviour and the interactions of the functional groups between resins and the test chemicals. The results indicated that differences in specific surface area among the three resins has an important impact on the Q_{max} of individual EOCs, and the interactions of the functional groups between resins and the test chemicals, such as van der Waals, Coulomb, π-π interaction and hydrogen bonding (H-bonding) were controlling the sorption behaviour of EOCs with different dominant interactions for the different EOCs.

The binding kinetics of resins gels showed that the uptake of test chemicals by each resin gel increased rapidly with time for the first hour, followed by a relatively slow increase. XAD18 and HLB resins could be more suitable for use as binding phases than SXLA for target EOCs because of the faster uptake rates. The uptake kinetics of all test chemicals by the three resin gels fits well with the pseudo-second-order model.

3.2.2 Performance of DGT with different resin gels

The performance of DGT devices with HLB, XAD18 and SXLA resins as binding agents was comparatively evaluated in the laboratory under different conditions of pH, IS and DOM. The results indicated HLB and XAD18-DGT were more stable (C_{DGT}/C_b within the range of 0.9-1.1) under different environmental conditions compared to SXLA-DGT. The DGT devices with XAD18 and SXLA resins were also deployed for 5 days for comparison with HLB-DGT.

XAD18 and SXLA-DGT could also accumulate the test chemicals linearly with the deployment time for the majority of test chemicals (except MEP and BHA, slow uptake of MEP by XAD18 and BHA by SXLA could be a possible reason), but less chemical was accumulated compared to HLB-DGT (agreed well with theoretical predictions). It indicated that HLB-DGT could be used for measurement of all 11 test chemicals in aquatic systems directly and accurately, while XAD18-DGT and SXLA-DGT may not suitable unless "effective" diffusion coefficients are used.

3.3 Analytical Methods for EOCs

To analyse the EOCs in wastewater and field DGT samples, it was necessary to have the reliable analytical method for the study of EOCs in complex matrices. This was conducted in **Paper III**, which included the optimisation of SPE extraction for water samples (binding gel extraction has been optimised in **Paper I**) and instrumental analysis of LC-MS.

3.3.1 Optimisation of SPE method for sample pre-treatment

Spiked river water samples were extracted under different pH conditions with different SPE cartridges and then eluted by various organic solvents to optimise the best SPE conditions for 20 EOCs in waters systematically. The optimised SPE procedures were as follow: 500 mL of water samples was acidified (pH = 2.5 using 2 M HCl), filtered (Whatman, GF/F filter, 0.7 μm) and spiked with 100 ng of ISs before extraction. The Supel-Select HLB cartridges was preconditioned with 10 mL mixture of ethyl acetate (EA) and ACN (50:50, v/v) and 10 mL MeOH followed by 10 mL MQ water, and the water samples were then introduced into the cartridges at the flow rate of ca. 3 mL min^{-1}. The sample bottle was then rinsed twice with two aliquots of 50 mL of 5 % (v/v) methanol in MQ water, and this was also passed through the cartridge. After loading, the cartridge was rinsed with 10 mL MQ water and vacuum dried for 20 min. The EOCs held on cartridges were finally eluted with 12 mL the mixture solvent (EA: ACN, 50: 50. v/v). Results showed that good SPE recoveries for the majority of the EOCs

could be achieved by the optimised SPE procedure, and the overall recoveries fell in to the range of 80-120% for the majority of EOCs.

3.3.2 Instrumental analysis

The EOCs in both wastewater and field DGT samples were detected by LC-MS in this thesis. The MS parameters were optimised for the most intense signal of the fragmentation products for each chemical. The most intense ion/ ion transitions were selected for quantification. The MS method was validated based on the linearity and range of calibration curves, accuracy and precision, matrix effects and detection limits of EOCs. Two different LC-MS systems, a LC-QqQ-MS and a LC-Q-Orbitrap-HRMS, were employed for the sample analysis for comparative purposes. The results showed that good linearity and method precision could be achieved for both instruments generally, but the LC-QqQ-MS system may be more stable for batch analysis of environmental samples as better linearity and smaller RSDs of replicate measurements for the majority of EOCs were observed for LC-QqQ-MS compared to LC-Q-Orbitrap-HRMS. The LC-Q-Orbitrap-HRMS system was more sensitive than the LC-QqQ-MS system with lower IDLs (2-23 times) for individual EOCs. Because of the availability of the instrument, LC-QqQ-MS was used for sample analysis for field studies (**Paper IV** and **V**) in this thesis.

3.4 Application of DGT for EOCs in Chinese WWTPs

The DGT sampler for *in situ* measurement of EOCs in waters was successfully developed based on laboratory tests of the performance under different conditions followed by field validation. The DGT sampler with HLB resin gel was then applied for studying the fate of EOCs in Chinese WWTPs (**Paper V**). Ten of the WWTPs located in Wuhan and Dalian of China were selected according to the starting year of operation, main treatment processes and the capacities of the WWTPs.

3.4.1 Occurrences of EOCs in WWTPs

All of the 20 analysed EOCs could be detected in the influent and primary effluent from at least one of the 10 WWTPs, 19 (except HEP) and 18 (except BUP and HEP) of them were found in secondary effluent and final effluent from at least one of the 10 WWTPs, respectively. In the raw influent, 15 of the selected EOCs could be found in all of the samples with average concentrations ranging from 21.5 (BUP) to 1795 (BPA) ng L^{-1}. In the primary effluent, 12 of the EOCs were detected in all the samples with average concentrations ranging from 26.7 (E1) to 1268 (BPA) ng L^{-1}. In the secondary effluent, 10 of EOCs were detected in all the samples with average concentrations ranging from 4.77 (E1) to 578 (BPA) ng L^{-1}. In the final effluent, only 5 of the EOCs were detected in all the samples with average concentrations ranging from 21.6 (MEP) to 586 (NP) n ng L^{-1}. Alkyl-phenols and BPA were the predominant EOCs in the wastewater, accounting for > 60% of the concentration proportion on average in the wastewater collected at all sampling 4 sites of WWTPs. All of 20 EOCs and 18 of 20 EOCs can be detected in the raw influent and the final effluent, respectively. The high detection frequency of EOCs in the wastewater (100% for in 15 of 20 EOCs in the influent and for 5 of 20 in the final effluent) and relatively high concentrations could cause concern of these EOCs in the aquatic environment.

3.4.2 Spatial variation of EOCs in WWTPs

No significant differences ($p > 0.05$) were observed for the majority (13 in 20) of EOCs in the raw influent of the WWTPs from the two cities (Wuhan and Dalian). In the final effluent, no significant differences ($p > 0.05$) were observed for 10 of the 18 EOCs in the final effluent among the WWTPs from the two cities. These results indicated the usage of these EOCs is similar in both cities. The usage of EOCs may vary with urbanisation levels because of the different habits between urban and sub-urban/rural areas. No significant differences ($p > 0.05$) were observed for the 11 of 20 EOCs in the raw influent of the WWTPs between urban and

sub-urban areas. In the final effluent, significant higher concentrations were observed for the majority of detected EOCs (12 of 18) in the final effluent of the WWTPs from urban area than from sub-urban area.

3.4.3 Removal of EOCs in WWTPs

The overall removal efficiency was calculated for 19 EOCs (except EE2, the detection frequency was less than 50%) from 10 WWTPs, which were detected from more than half of the raw influent samples. High levels of overall removal were observed for parabens ranging from 81 to 100%. Good removals (average > 50%) were also observed for oestrogens (except DES), BPA, OPP and TCS. Relatively low removal rates (< 50% on average) were observed for the alkyl-phenols, antioxidants, DES and TCC. The average removal of PHBA cross the 10 WWTPs was < 0%, since it a metabolite of parabens and can be produced during the degradation of parabens. The contribution of each treatment process/technique to the overall removal within a single WWTP was assessed by the relative removal efficiency for each treatment unit. The average relative removal efficiency of individual TOrCs for primary, secondary and final treatment in 10 WWTPs ranged from -57 to 100%, 23 to 141%, and -23 to 133%, respectively. The primary and secondary treatment units contributed to the most removal of the TOrCs. Especially for antioxidants and alkyl-phenols, the secondary treatment is the key process to remove these compounds. The final treatment of disinfection as well as the microfiltration, sand filter and etc. is ineffective on the removal of the TOrCs.

4. Conclusions and Future Perspectives

4.1 Conclusions

The main conclusions delivered from the studies undertaken in this thesis (**Paper I-V**) can be summarized as follows:

1) The principle of DGT has been successfully applied for several groups of EOCs with HLB resins as the binding agent and agarose gel as the diffusion layer, confirming the potential of DGT for sampling wide range of organic chemicals in the aquatic environment.

2) It is important to select suitable resin to be the binding phase when developing the DGT sampler. The resin properties and the interactions of functional groups between the resin and chemicals control the uptake of EOCs for DGT sampler.

3) The DGT sampler for EOCs has been validated under the real world condition-WWTP by deploying the devices in both influent and effluent. It showed that DGT samplers could provide comparable results to auto-samplers, with simpler sample pre-treatment for DGT and less matrix interference in the DGT samples. 7-18 days' deployment was shown to be practical for field studies taking into consideration of the detection limits and avoiding fouling effects.

4) The effects of the DBL were shown to be relatively limited compared with other passive samplers for organic chemicals, and the effects could be estimated by simultaneously deploying the DGT devices with different thicknesses of diffusion layer for the same time period.

5) A sensitive analytical method has been developed for the simultaneous determination of EOCs in surface water and wastewater by SPE extraction followed by LC-MS analysis. This method has been shown to provide reliable data for the samples with

complex matrices and could achieve low enough detection limits for EOCs quantification.

6) DGT samplers can be effective and simple tools to study the fate of EOCs in wastewater. DGT devices with HLB resin gels were applied in 10 WWTPs in China to study the fate and removal efficiencies of EOCs. All target EOCs could be found in the raw influent and majority of them could still be detected in the final effluent. Removal of the EOCs varies for different EOCs.

4.2 Recommendation and Perspectives

Due to the large amounts of the EOCs discharged into the environment via WWTPs, it is important to know their fate, behaviour and removal in the WWTPs and to assess the risks after entering the environment. The study in this thesis tried to investigate their fate in WWTPs with the assistant of DGT passive samplers. Owing to the advantages of DGT sampler, large scale studies could be easily conducted in the future.

This thesis only focuses on the aqueous EOCs in the wastewater from the WWTPs, however, the sludge is also an important to affect the fate and behaviour of EOCs in WWTPs. The DGT sampler could also been potentially applied for measuring the EOCs in the sludge, providing full scale study on the fate of EOCs in the WWTPs, together with its deployment in the wastewater.

The DGT could perform well for the majority of EOCs and under various environmental conditions, but not good enough as the theoretical prediction (C_{DGT}/C_b <0.8) for some chemicals (such as TCS) and under some conditions (such as seawater with high IS). Thus, the further calibration or configure of the DGT devices may be still needed, so that DGT could be applied for wide range of chemicals and conditions.

Modelling is also a useful tool to study the fate and risk of EOCs in wastewater. Combining with the results from DGT samples, the input data of the models could be improved and uncertainties should be reduced. Thus, models could provide more accurate results on EOC fate and risk assessment, which will be helpful to the decision makers.

The study of the bio-transformation and metabolism of EOCs in wastewater can also be interesting because some bio-transformation and metabolism products of the EOCs may be pose greater risk then parent products. Combining with the DGT samplers, bio-transformation and metabolism of EOCs in the wastewater could be studies *in situ* during the deployment period.

DGT technique, as an emerging and promising tool for studying the fate of EOCs in aquatic environment, can be expected to be applied to other groups of EOCs with the availability of new resin materials. For example, the application of MIP resin techniques could be helpful for DGT sampler to uptake the target chemicals with high selectivity and further reduce matrix interferences/co-existing substances.

Beyond use as a sampling method, DGT passive sampling also could be potentially applied to study other aspects on environmental and toxicological research, such as screening of illegal discharge of industrial compounds into the aquatic environments, the target or non-target screening of unknown contaminants coupled with HRMS and bioavailability of emerging contaminants by simplifying procedures and reducing the need for animal tests.

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Paper I

Development of DGT Passive Sampling Technique for *in situ* Measurements of Trace Organic Chemicals Discharged in Household Wastewater

Development of DGT passive sampling technique for *in situ* measurements of trace organic chemicals discharged in household wastewater

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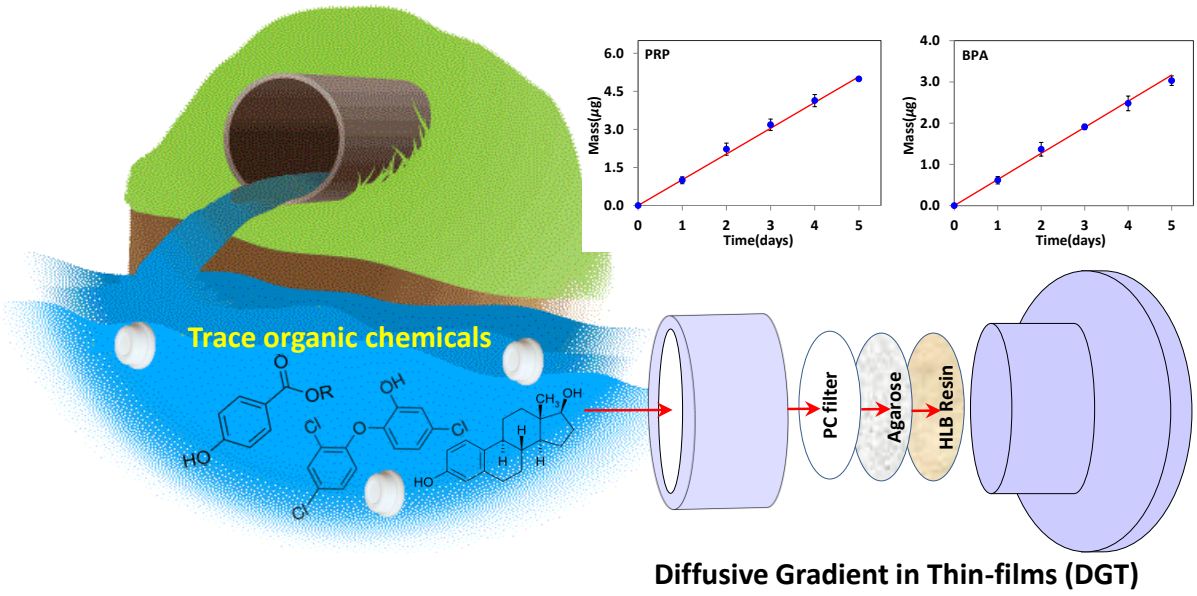

Trace organic chemicals
PRP
Mass(μg)
Time(days)
BPA
Mass(μg)
Time(days)
PC filter
Agarose
HLB Resin
Diffusive Gradient in Thin-films (DGT)

ABSTRACT:

Widespread applications of organic chemicals in consumer products and their continuous discharge into aquatic environments has led to their ubiquitous detection, which may pose risks to organisms and humans. Reliable, robust techniques to monitor environmental concentrations are therefore required. The passive sampling approach of diffusive gradients in thin films (DGT) is demonstrated to provide *in situ* quantitative and time-weighted average measurement of these chemicals in aquatic systems. A novel DGT sampler using hydrophilic-lipophilic-balanced (HLB) resins as binding agent was developed and tested for a selected group of compounds, including preservatives, oestrogens, antioxidants and disinfectants. Ultrasonic extraction of resin gels in 5 mL acetonitrile gave good and consistent recoveries for all 11 test chemicals. Uptake by DGT was relatively independent of pH (3.5-9.5), ionic strength (0.001-0.1 M) and dissolved organic matter (0-20 mg L^{-1}). Time and diffusion layer thickness dependence experiments confirmed DGT accumulated chemicals consistent with theoretical predictions. DGT samplers were deployed in a wastewater treatment plant and results compared with grab-samples and 24-hour-composited samples from auto-samplers. Field application demonstrated the superiority of the DGT technique for organic chemical measurements in aquatic systems, giving *in situ* analyte pre-concentration in a simple matrix for analysis, with high accuracy and low detection.

1. INTRODUCTION

Household consumers use a range of home and personal care products and pharmaceuticals that contain a broad range of trace organic chemicals[1] (TOrCs, including preservatives, antioxidants, disinfectants, oestrogens, etc.) that are designed to enhance the quality of their lives.[2] Consumer spending power and the availability of these products continues to increase, thus the global production and usage of many of these chemicals has continued to increase. For example, >10 million tonnes of pharmaceuticals were sold globally in 2012 and there was 213 billion USD of personal care product sales in 2013 all over the world (estimated from ESRI 2012[3] and ChinaIRN 2012[4]). The organic chemicals used in these products can potentially enter the environment via wastewater treatment plants (WWTPs) or direct discharge of household wastewater,[5] and are typically considered to constantly be emitted via wastewater streams.[6] The polar, non-volatile nature of the majority of chemicals used in these products will result in their distribution and transport primarily into the aquatic environment.[7] The possible adverse effects[7] on aquatic organisms of some chemicals, such as endocrine disrupting effects[8] and toxicity[9] is a potential concern.

Monitoring organic chemical concentrations is an essential aspect for studying their fate and behaviour in aquatic environments,[10] providing data to evaluate potential risks to ecosystems and human health. Passive water sampling has seen a remarkable rise both in availability and popularity for monitoring programmes,[11, 12] although conventional sampling methods, such as discrete grab sampling, are still considered as the ‘gold standard’.[13] However, passive samplers, in comparison with conventional methods (grab, auto-samplers, etc) offer a number of distinct advantages. For example, passive samplers

provide an *in situ* technique which accumulates the freely dissolved fraction of the target analytes without affecting the bulk solution, providing either equilibrium or time-weighted average (TWA) concentrations.[11, 14] *In situ* pre-concentration by passive sampling can provide increased sensitivity[14] and reduce/eliminate the matrix interferences and solvent consumption.[15] It can minimise sample contamination (it is pre-selective), decomposition/degradation or loss/change in post-sampling transport and storage.[14] It can also provide an economical and effective solution to contaminant sampling because of its simple design, operation and treatment.[16] Some passive water samplers, designed for trace organic pollutants (e.g. semipermeable membrane devices (SPMD), polar organic chemical integrative sampler (POCIS) and Chemcatcher), require *in situ* and/or laboratory calibration data,[11, 17] where calibration is dependent on the hydrodynamic conditions such as water flow.[18, 19] Such factors can result in considerable measurement uncertainty.[11, 17] Therefore, performance reference compounds (PRCs) are used to provide calibration data to assess the difference between the *in situ* sampling rates (R_S) and laboratory derived values,[17, 20, 21] but it is still problematic for polar chemicals.

The passive sampling technique of diffusive gradients in the thin films (DGT) has been demonstrated to provide quantitative *in situ* measurements of trace chemicals in aqueous systems.[22] Unlike other passive samplers, *in-situ* calibrations are not necessary for DGT, as the transport of the analyte is solely controlled by its molecular diffusion.[22, 23] The principle of the DGT sampler, based on Fick's first law of diffusion, has been reported previously.[22, 24] The DGT measurement, C_{DGT}, provides the TWA concentrations of organics in the solution, which is expressed using the equation (1.1):[22]

$$C_{DGT} = \frac{M(\Delta g + \delta)}{D_e A t} \quad (1.1)$$

$$\text{or}\quad C_{\mathrm{DGT}} = \frac{M\Delta g}{D_{\mathrm{e}} A t} \tag{1.2}$$

where M is the measured mass of target chemical accumulated in the binding gel, Δg is the thickness of the diffusive layer, δ is the thickness of diffusive boundary layer (DBL), D_{e} is the diffusion coefficient of target chemical, t is the exposure time and A is the exposure window area of the cap. Δg is much thicker than the typical thickness of DBL under most conditions so that the influence of the DBL becomes negligible, making the DGT measurement fairly insensitive to hydrodynamic conditions,[22, 24] so Equation (1.1) can be simplified to version (1.2).

Theoretically, DGT can be applied to any inorganic or organic diffusing species,[23] although most research has been focused on the measurement of inorganic substances,[24] showing that this technique has been well established and widely applied to monitor inorganic components.[24, 25] More recently, a few attempts have been made on the measurements of organic substances. For example, Chen *et al.*[16, 26, 27] successfully extended the application of DGT using XAD18 as the binding resin to measure antibiotics in waters and soils. Dong *et al.*[28, 29] subsequently used this sampler with molecularly imprinted polymers (MIP) as the binding agents to sample phenol and 4-chlorophenol (4-CP) in water. Zheng *et al.*[30] successfully applied DGT to bisphenols (BPs) using activated charcoal as the binding layer and Fauvelle *et al.*[31] applied titanium dioxide (TiO_2) as binding phase for DGT to detect glyphosate (PMG) and aminomethyl phosphonic acid (AMPA) in the aquatic environment. Thus, the possibility of a DGT sampler for measurement of other chemicals, such as preservatives, oestrogens, antioxidants and disinfectants, which are widely-used in home and personal care products and pharmaceuticals,[32] is of great interest.

Therefore, the aim of this study was to develop a novel DGT sampler for measurement of a wide range of organic chemicals in waters, including preservatives, oestrogens, antioxidants and disinfectants. Eleven different chemicals were used here as test chemicals to: 1) systematically test the performance of this DGT under different laboratory conditions, with various pH values, ion strength (IS) and dissolved organic matter (DOM) contents, 2) investigate the effect of DBL on the accuracy of *in situ* measurement, 3) validate this sampler using data of time and diffusion layer thicknesses dependence on uptake kinetics and 4) assess the applicability of DGT under realistic conditions by a field testing trial in a WWTP.

2. METHODS AND MATERIALS

2.1 Chemicals and Reagents

High purity standards of 11 test chemicals, methylparaben (MEP), propylparaben (PRP), isopropylparaben (IPRP), bisphenol-A (BPA), estrone (E1), *β*-estradiol (E2), estriol (E3), 17α-ethinylestradiol (EE2), butylated hydroxyanisole (BHA), ortho-phenylphenol (OPP) and triclosan (TCS) were purchased from Sigma-Aldrich (UK). Detailed information of these test chemicals is provided in the Supporting Information (SI) **Table S1**. Stock solutions of each test chemical standard (1000 mg L^{-1}) were prepared in methanol and stored in sealed amber bottles in the dark at -20 ℃ for later use. Working standard solutions (10 mg L^{-1}) were prepared weekly by diluting the stock solutions with methanol and stored at 4 ℃ before use. Hydrophilic-lipophilic-balanced (HLB) resins were extracted from Oasis-HLB SPE cartridges purchased from Waters Corporation (UK). The resins were thoroughly washed with Milli-Q (MQ) water and then immersed in methanol followed by MQ water wash before use. Information on the reagents used in the experiments can be found in **SI**. Detailed description of

experimental controls, including the plastic-ware and glassware clean-up, pH and temperature measurement, the adjustment of pH, IS and DOM concentration in the water solution, the sampling frequency, blank and control experiments setting, result data expression and statistical analysis and other setting is provided in the **SI**.

2.2 Diffusive and Binding Gel Preparation

Polyacrylamide diffusive gels (PA, 1.0 mm), agarose diffusive gels (AG, 1.5 % agarose, different thicknesses) and binding gels (0.4 mm, HLB as binding resin) were prepared according to well documented procedures.[33-35] All gel sheets were washed in 1 L MQ water and hydrated in another 1 L MQ water for about 24 hours (h). The water was changed 3-4 times until pH was below 7. The sheets were then cut into 2.5 cm diameter disks and stored in 0.01 M NaCl solution at 4 ℃ before use.

2.3 Chemical analysis and Detection Limits

A Thermo Finnigan high performance liquid chromatography (HLPC) coupled with a photodiode array detector (DAD) was employed to analyse the 11 test chemicals in both water and DGT samples for all the lab experiments (details provided in **SI**). Wastewater[39,40] and field DGT sample pre-treatment and liquid chromatography- mass spectrometer (LC- MS) analysis[36, 37] for these field samples (both DGT and water samples) was optimised and conducted according to published procedures (details of the information on the pre-treatment and the instrumental analysis given in **SI**).

The instrumental detection limits (IDLs) for LC-DAD and LC-MS were calculated based on the signal/noise ratio (S/N) >3 and method detection limits (MDLs) were calculated based on IDLs, the concentration factors and the absolute recoveries for water samples and DGT samples. **Table 1**

summarises the IDLs of test chemicals for LC-DAD and LC-MS instruments and the MDLs of these chemicals for both water and DGT samples during the lab experiments and the field application (Details of the MDLs calculation are given in **Table S2**).

Table 1 IDLs of test chemicals for LC-DAD and LC-MS, and MDLs of test chemicals for both lab and field samples.

Test	IDL, ng mL^{-1}		Lab MDL, ng mL^{-1}		Field MDL, ng L^{-1}	
Chemicals	LC-DAD	LC-MS	Water	DGT	Water	DGT
MEP	1.16	0.48	2.32	0.52	0.52	0.51
IPRP	1.43	0.32	2.86	0.74	0.35	0.39
PRP	1.64	0.37	3.28	0.84	0.41	0.45
E1	2.17	2.54	4.34	2.33	2.76	6.49
E2	2.04	3.65	4.08	2.42	3.98	10.33
E3	1.82	2.37	3.64	1.43	2.58	4.44
EE2	2.35	4.03	4.70	2.29	4.38	9.35
BPA	1.79	0.77	3.58	1.36	0.84	1.39
BHA	1.87	1.56	3.74	2.54	1.79	5.31
OPP	1.55	2.99	3.10	1.16	3.26	5.33
TCS	1.91	0.87	3.82	2.23	0.95	2.41

2.4 Performance Test of DGT in the Laboratory

2.4.1 Adsorption by DGT holder, diffusive gels and membrane filters

Materials which were used for making DGT devices were assessed for possible adsorption of test chemicals. The plastic DGT holder (piston and cap), two diffusive gels (PA and AG), five membrane filters (polyethenesulfone membrane, PES; cyclopore track etched membrane, PC1; Nuclepore track-etch membrane, PC2; Nuclepore polycarbonate membrane, PC3; cellulose nitrate membrane, CNM; details given in **SI**) were immersed in solution containing 100 μg L^{-1} of test chemicals and shaken for 24 h on a shaker (Orbital, DOS-20L, Sky Line, ELMI). The amounts of test chemicals adsorbed by these materials

were calculated using the mass balance based on concentrations in the solutions before and after experiment.

2.4.2 Optimisation of extraction recoveries

The recoveries of test chemicals in this study were defined as the ratios of measured chemical in the extracts from HLB binding gels to the chemical adsorbed by the binding gel. HLB gels were added into 10 mL solution of 250 μg L^{-1} test chemicals and shaken for 24 h on the shaker. The binding gels were then taken out for ultrasonic extraction. The amounts of test chemicals adsorbed by binding gels were obtained from the mass balance using the concentration difference before and after the experiment. To optimise the extraction efficiency, HLB binding gels (already adsorbed the test chemicals) were placed into 15 mL vials with 5 mL solvent (ACN or MeOH) added each time, and then ultrasonically extracted for 15 or 30 min with either one or two extractions. Once the extraction method is optimised, the recoveries were tested at two further concentrations (ca. 100 and 500 μg L^{-1}) to confirm whether the stable recoveries could be achieved with a wide range of exposure concentrations.

2.4.3 Uptake capacity of DGT and binging gel uptake kinetics

The DGT devices (a 0.4 mm resin gel in the front of a 1.0 mm diffusive gel) were used for assessing the uptake capacities of DGT for 11 test chemicals. The devices were exposed to 50 mL solutions of various concentrations of test chemicals up to ca. 10 mg L^{-1}. All the solutions (pH = 6 or 8) were shaken for 24 h at room temperature (20±2 ℃). The adsorbed amounts of test chemicals by resin gels were calculated according to the concentration differences before and after the experiment.

Uptake kinetics of test chemicals by HLB binding gel was investigated by immersing gel discs in

solutions for different times. Gel discs were placed and shaken in 20 mL of 200 μg L^{-1} test chemical solutions (IS=0.01 M and pH=6.8±0.1), and 0.1 mL samples were collected each time for a period of 24 h at room temperature (20 ± 2 ℃).

2.4.4 Diffusion coefficient measurements

A diffusion cell containing two compartments (source and receptor) connected by a circular window (1.5 cm diameter) with a 0.8 mm diffusive gel (AG gel without filter) was used to measure the diffusion coefficients (D_e) of test chemicals according to a published procedure.[33] Both compartments were filled with 100 mL of 0.01 M NaCl solution (pH = 6.8 ± 0.1). 11 test chemicals were spiked into the source compartment (ca. 3000 μg L^{-1} for each chemical). The solutions in both compartments were well-stirred during the experiment. Samples (0.1 mL) from both compartments were collected and analysed by HPLC-DAD at intervals of 60 min for the first 3 h and then subsequently at 30 min intervals for the next 8-9 h. The slope (k) of the linear plot of the test chemical mass (M) diffused into the receiving compartment *versus* the time (t) of the measurement can be used to calculate D_e, according to Equation (2) below:

$$D_e = \frac{k\Delta g'}{C_s A_s} \quad (2)$$

where C_s is the test chemical concentration in the source solution, A_s is the window area of the diffusion cell, and $\Delta g'$ is the thickness of the diffusion gel. The experiments were conducted in a temperature-controlled room at three different temperatures of 15, 20 and 25 ℃ (the temperature change during the experiment was less than 0.5 ℃).

2.4.5 Effect of pH, IS and DOM

The pH, IS and DOM of solution can potentially affect DGT performance by changing the chemical speciation in the solution and/or the rate and efficiency of binding. Thus, the performance of DGT was tested at a wide range of pH (3.5-9.5), IS (0.001 M – 0.5 M) and DOM (humic acid, 0-20 mg L^{-1}). The DGT devices were deployed in 2 L of 100 μg L^{-1} test chemical solutions (20±2 ℃) for 20 h with a stirring speed of 350 rpm by a magnetic stir bar. The DGT-measured concentrations (C_{DGT}) of test chemicals were calculated using Equation (1.2), and the ratio of C_{DGT} to the directly measured concentration (C_b) of test chemicals in the bulk solution was used to evaluate the performance of DGT under different conditions. The ratio of C_{DGT}/C_b ranged from 0.9 to 1.1 indicating the excellent performance of DGT.

2.4.6 Effect of flow velocity

The effect of flow velocity on DGT measurement was tested. Five stirring rates were set from 0 to 900 rpm to simulate the different water flow velocities. The DGT devices were deployed in 2 L of 100 μg L^{-1} test chemical solutions (IS = 0.01 M, pH = 6.5±0.1 at 23±2 ℃) for 24 h. After retrieval, the resin gel was extracted and analysed for the test chemicals.

2.4.7 Time and diffusion layer thickness dependence

DGT devices were deployed into solution (IS = 0.01 M, pH = 6.8±0.2 at 24±2 ℃) of ca. 50 μg L^{-1} test chemicals for different durations (up to 5 days (d)) at stirring speed of 350 rpm. After deployment, all DGT devices were rinsed with MQ water thoroughly before disassembly. The filter and diffusive gel layers were peeled off, and the resin gel layer was extracted for test chemicals using the optimised procedure in *section 2.4.2*. Quantification of test chemicals accumulated in binding gels was then

211 determined.

212 DGT devices with various thicknesses of diffusive gels (0.5 to 2.0 mm) were used to test the DGT
213 principle for accurately measuring test chemicals. The DGT devices were deployed in solution (IS = 0.01
214 M, pH = 6.8±0.2 at 24±2 ℃) of ca. 60 μg L^{-1} test chemicals for 20 h at a stirring speed of 350 rpm. After
215 the experiment, the test chemicals in the resin gels were extracted and analysed.

216 ### 2.5 Application in WWTP

217 To test the applicability of DGT in the field conditions, DGT devices were deployed *in situ* at a WWTP in
218 the UK. The devices were located ca. 30 cm below the water surface in influent and effluent channels for
219 up to 2 weeks. The average water temperature was 9.6 ℃ during the deployment. DGT samplers were
220 retrieved at Day 4, 7, 10 and 14 from each site, rinsed with MQ water and then sealed in a clean plastic
221 bag for transport. On arrival at the laboratory, the DGT binding gels were taken out and extracted. During
222 the period of deployment, active water samples including both grab-samples (at about 10 am) and
223 auto-samples (24-h composite) were also collected on Day 1, 7 and 14. Field blank samples of DGT were
224 also prepared and taken to the WWTP without deployment. Detailed information on wastewater and field
225 DGT sample pre-treatment and LC- MS analysis is given in the **SI**.

226 ## 3. RESULTS AND DISCUSSION

227 ### 3.1 Adsorption by DGT Holder, Diffusive Gels and Membrane Filters

228 The results of the adsorption experiment (**Figure S1**) demonstrated that there was no significant
229 adsorption (ANOVA, $p > 0.05$) by the DGT holders for all the 11 test chemicals. No significant adsorption

by PA or AG was observed, while AG had better stability. PES filters used for POCIS and Chemcatcher[38] and CNM filters, were demonstrated to adsorb all the 11 test chemicals significantly (nearly 100% absorbed by PES and 50% by CNM), while moderate adsorption was observed for PC1 filters (34%) and PC3 filters (12%) and very slight adsorption by PC2 filter (< 5% on average). Thus, AG gel (1.0 mm, 1.5%) and the PC2 filter were selected as the diffusive gel and filter in the subsequent experiments.

3.2 Optimization of Extraction Recoveries

Extraction of binding gel with ACN showed better recoveries for E1, E2, E3, EE2 and BPA than with MeOH (<60%), so ACN was chosen for this study. Optimisation of the extraction procedure demonstrated that, for most of the test chemicals, the average recoveries of extraction were in the order: a single 15 min extraction < two 15 min extractions < one 30 min extraction < two 30 min extractions (**Figure S2**), but there were no significant differences (ANOVA, p>0.05) between a single and multiple 30 min extractions. Thus, a simple procedure of a single 30 min ultrasonic extraction by 5 mL ACN was selected as the extraction method, which provided good recoveries ranging from 66.0±7.3 % (E1) to 122±3.4 % (IPRP). The variations of the recoveries among chemicals could be results from the extraction efficiency or matrix interferences.

The test chemical recoveries of the batch extraction using the optimised procedure were investigated at three different concentrations (100, 250 and 500 μg L^{-1}), to test recovery stability when different amounts of test chemicals are adsorbed in the resin gels. The results demonstrated that test chemical recoveries at all three concentrations in HLB binding gels were not significantly different (**Table S3**). The overall average recoveries (calculation of three different concentrations together, data listed in **Table S3**) ranged

from 64.6±5.0% (BHA) to 123±11.1% (IPRP).

3.3 Binding Capacity of DGT and Uptake Kinetics of Binding Gel

The results obtained from the uptake experiments demonstrated that the uptake of all test chemicals increased linearly at relatively low concentrations of solution for HLB resin gel at both pH 6 and 8, and no significant difference was observed between the two pH systems. With increasing solution concentration, the uptake-mass continued to accumulate but the uptake rate slowed, and differences appeared between pH 6 and 8 (**Figure S3)**. However, after the linear phase, the uptake mass was larger at pH 6 than at pH 8 for the majority of test chemicals, indicating that HLB gel has a greater binding capacity under lower pH conditions. This could be 2 reasons: 1) the more neutral fraction of TOrCs in the acid condition lead them to be adsorbed by HLB. 2) HLB has better adsorption for chemicals under acid condition suggested by the manual of HLB.[39] Exceptions included EE2 and TCS, which were linearly taken up by HLB binding gel in both pH 6 and 8 solutions during the whole period of experiments and the whole range of the concentrations, indicating that these two chemicals did not reach the accumulation capacities of the resin in this experiment.

The linear phase uptake curves were used to estimate the maximum linear accumulation capacities of HLB resin gels for test chemicals, and the results are shown in **Table S4**. The capacities (based on the lowest results from both pH values) ranged from 11.8 (MEP) to more than141 μg (EE2) per gel. Based on the estimated capacity, the maximum water concentrations measured by DGT deployed for 2 weeks, were calculated using Equation (1) and ranged from 45.5 (MEP) to more than 1100 μg L^{-1} (EE2). Where DGT devices were deployed for 1 month, the maximum water concentrations ranged from 21.2 (MEP) to >510

μg L^{-1} (EE2). The concentrations of test chemicals in waters would be less than 10 μg L^{-1} in most cases, so projected maximum deployment times would be ca. 2 months (MEP) to ca 1 year (EE2). However, considering the coexistence of other adsorbed chemicals and the possibility of biofouling in the aquatic environment, shorter deployment times (eg. ≤1 month) are recommended.

The results of binding kinetics (**Figure 1**, full set in **Figure S4**) demonstrated that the uptake of test chemicals by HLB resin gel increased rapidly for the first hour (ca. 60% uptake), followed by more gradual uptake. The rapid initial uptake is the key aspect to enable good performance of DGT samplers, obeying Fick's law. Complete uptake of the majority of test chemicals was obtained within 12 h for HLB gel, and of all test chemicals in 24 h, which indicated that HLB gel is suitable for use as the binding phase.

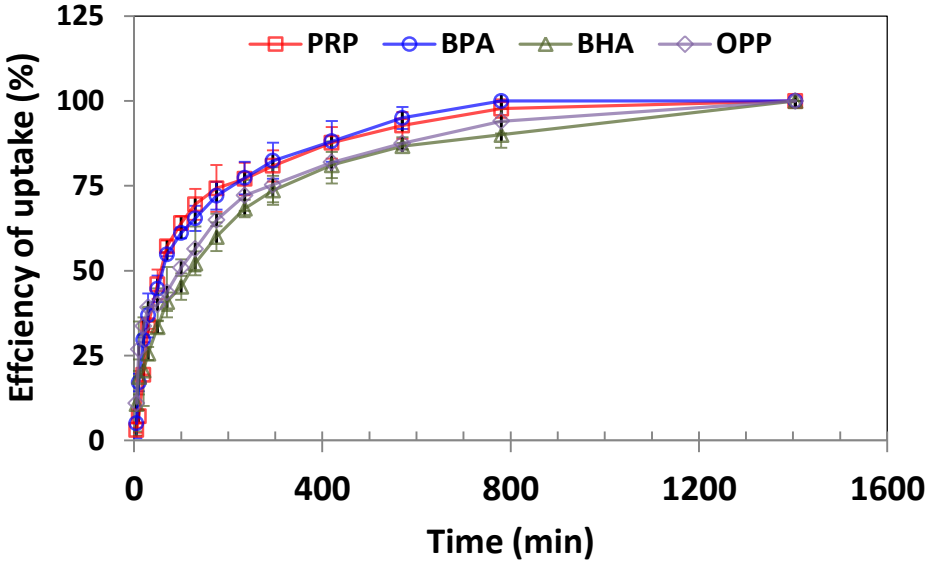


Figure 1: Dynamic binding of selected test chemicals by HLB resin gels in 20 mL solutions of 200 μg L^{-1} test chemicals (IS = 0.01 M, pH = 6.8±0.1, T = 20±2 ℃; n=3). Error bars were calculated from the standard deviation (SD) of three replicates.

3.4 Diffusion Coefficient Measurement

It is necessary to know the diffusion coefficient (D_e) of the chemical in the diffusive gel to calculate the water concentration using Equation (1.1 or 1.2). In theory, D_e is temperature dependent and can be measured independently using a diffusion cell device in the laboratory. The D_e of test chemicals at 25℃ (D_{25}) were calculated using the Equation (2), based on the k values obtained from **Figure S5** and data are given in **Table 2**. The D_e values at additional temperatures (D_T) can be estimated using Equation (3), and D_e values from 1 to 35℃ were calculated and listed in **Table S5**.

$$\log D_T = \frac{1.37023(T-25)+8.35\times10^{-4}(T-25)^2}{109+T} + \log\frac{D_{25}(273+T)}{298} \quad (3)$$

Measurements at 15 and 20℃ were also carried out to compare with the calculated values, it was demonstrated that the measured D_e at both 15 and 20℃ compared well with the calculated ones, which differed within 10%. A recent DGT study on BPA demonstrated that the D_e was 4.71 E-06 cm^2 s^{-1} (IS = 0.01 M, pH = 7, 25℃),[30] which is <2% different to results presented here, indicating the accuracy of D_e measurement in this study.

The sampling rate per unit area ($R_{S/A}$) for DGT was estimated by Equation (4)[16] in order to compare with other passive samplers. $R_{S/A}$ values of a DGT device (1mm diffusive layer) for test chemicals at 25℃ are given in **Table 2** and ranged from 2.97 to 5.95 mL (d cm^2)$^{-1}$. These are similar and comparable with reported $R_{S/A}$ for POCIS and Chemcatcher, indicating that the DGT sampler can be used for measuring trace organic chemicals in the aquatic environment.

$$R_{S/A} = \frac{D_e}{\Delta g} \quad (4)$$

Table 2: D_e (E-06 cm^2 s^{-1}) and $R_{S/A}$ (mL (d cm^2)$^{-1}$) at 25 ℃ for DGT and some available $R_{S/A}$ for other passive samplers.

Sampler	MEP	PRP	IPRP	E1	E2	E3	EE2	BPA	BHA	OPP	TCS
DGT D_e	6.85	5.92	5.91	4.80	3.58	4.59	3.40	4.80	4.25	5.18	3.63
DGT $R_{S/A}$	5.9	5.1	5.1	4.2	3.1	4.0	2.9	4.1	3.7	4.5	3.1
POCIS $R_{S/A}$	-[a]	-	-	0.39[40]-19[41]]	0.31[40]-17[41]	0.41[40]-6.0[21]	4.5[42]-18[43]	1.3[21]-18[43]	-	-	26[41]-42[44]
Chemcatcher $R_{S/A}$	-	-	-	8.0[45]	10[45]	-	-	6.5[45]	-	-	-

a: no data available.

3.5 Effect of pH, Ionic Strength and DOM

3.5.1 Effect of pH

Figures 2a and **S6** show the effect of solution pH on DGT uptake of test chemicals in solution. For the majority of test chemicals, C_{DGT}/C_b was stable between 0.9 and 1.1 when pH ranged from 3.5 to 9.5 (the averages of C_{DGT}/C_b values at all pH for individual chemicals were in the range of 0.97-1.08, data list in **Table S6**). No significant difference (ANOVA, p>0.05) of the C_{DGT}/C_b was observed, although there was a slight decline of C_{DGT}/C_b at the highest pH (9.5). The only exception of small values of C_{DGT}/C_b was observed for TCS (**Table S6**): the C_{DGT}/C_b values at all pH were <0.90, but no significant difference (ANOVA, p>0.05) of the C_{DGT}/C_b was found among different pH values (0.85 on average). Possible reasons for C_{DGT}/C_b decline with increasing pH could include: 1) the HLB resin has strong retention and binding of organic chemicals in acid conditions[39] and 2) the anionic proportion of test chemicals was weakly retained and less bound to the HLB resin gels because of electrostatic repulsion[46] at higher pH conditions (these chemicals are ionizable and the neutral fraction decreased with increasing pH). Similar phenomena have previously been observed when HLB-POCIS was used for endocrine disrupting

chemicals (EDCs including E1, E2, EE2 and BPA) measurement,[42] and DGT was used to measure antibiotics,[26] 4-CP[29] and BPs[30] in water. These findings demonstrated that the DGT performance is generally independent of solution pH for the majority of test chemicals and it can be directly applied to their measurements in most of the field conditions with wide range of pH values.

3.5.2 Effect of IS

The effect of IS on DGT performance for 11 test chemicals is shown on **Figures 2b** and **S7**. No significant differences (ANOVA, p>0.05) were observed for the majority of test chemicals when the IS concentration was 0.001-0.1 M, and values of C_{DGT}/C_b fell between 0.9-1.1 (data in **Table S6**), except for BHA and TCS. A significant reduction in C_{DGT}/C_b (>10%) was observed when IS increased to 0.5 M. The possible reason for the decline was that the test chemicals were less bound to the resin gels due to the competition with other major ions (e.g. Cl^-). A similar phenomenon was previously observed when XAD18 was used as the resin for antibiotics,[26] when uptake to the binding gel decreased with increasing IS. This result is also consistent with Togola and Budzinski's study on POCIS uptake of pharmaceuticals[47] and Zheng *et al.*'s study on DGT performance for BPs when IS increased to 0.5 M.[30] However, the results are not consistent with Zhang *et al.*'s study of HLB-POCIS on EDCs where R_S did not vary significantly with changing salinity from 0-3.5%[42] and also contrasts with Dong *et al.*'s research on 4-CP; they demonstrated that the ratio of C_{DGT}/C_b increased when IS concentration increased from 0.1 to 0.7 M.[29] Our results indicate that the DGT is suitable for use in freshwater but not in seawater unless the IS effect is further calibrated in future.

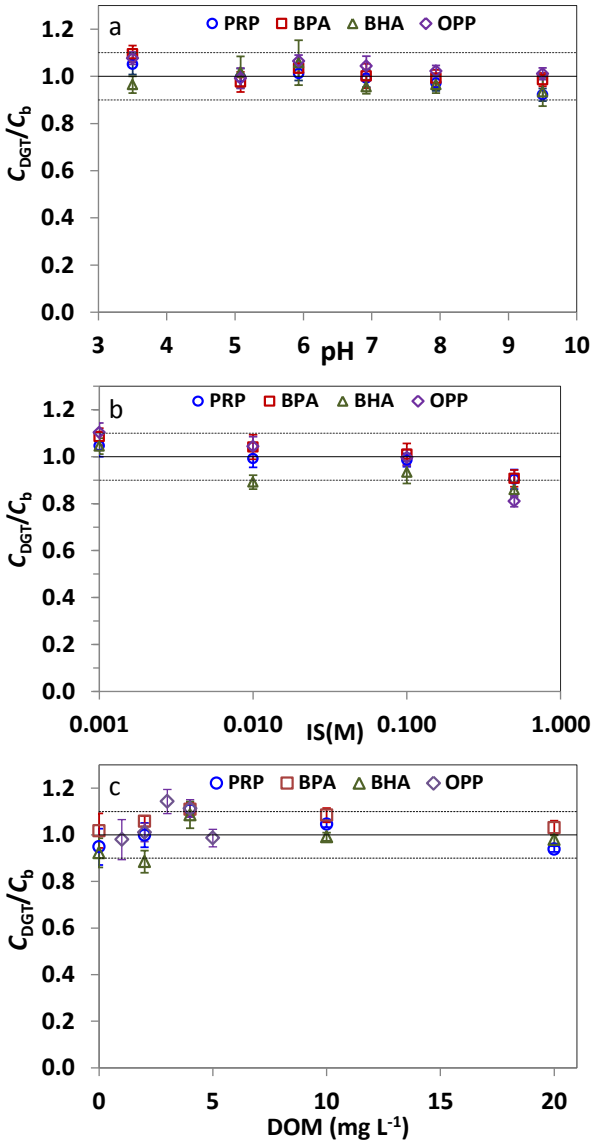


Figure 2: Effect of pH (a), IS (b) and DOM (c) on HLB-DGT measurement (n = 3) for example chemicals. The solid horizontal lines represent the value of 1 and the dotted horizontal lines represent the values at 0.9 and 1.1. Error bars: 1SD.

3.5.3 Effect of DOM

Figures 2c and S8 demonstrate the effect of DOM on DGT measurement for all the test chemicals. The ratios of C_{DGT}/C_b for most test chemicals are within the range of 0.9-1.1, except for TCS, when the DOM concentrations increase from 0 to 20 mg L^{-1}. The ratios did not significantly change (ANOVA, $p>0.05$) for

the majority of test chemicals over the test range of DOM. The ratios of C_{DGT}/C_b for TCS were always < 0.9 and kept on decreasing with the increase of DOM concentration. This result for the majority of test chemicals is consistent with Charlestra *et al*'s[19] study on pesticides uptake by HLB-POCIS with varying dissolved organic carbon (DOC) contents who demonstrated no significant differences when DOC was between <0.1 and 4.51 mg L^{-1}. In addition, Li *et al.*'s study[41] demonstrated an increase in uptake of polar organic chemicals (POCs) by HLB-POCIS when DOM increased from 3.33 to 4.92 mg L^{-1}. However, Dong *et al*[29] demonstrated reduced ratios of C_{DGT}/C_b for 4-CP at high DOC contents (9.8-36.5 mg L^{-1}), which was similar with the result for TCS from our study. These results indicated that HLB-DGT performed well for the majority of test chemicals when the DOM concentration was varied and it can be applied in the aquatic environment with a wide range of DOM.

3.6 Effect of DBL

The DBL can affect the accuracy of DGT measurement. It exists between solid and liquid interfaces (membrane and solution for DGT) and cannot be eliminated thoroughly. But the effect could be reduced by proper experimental design,[48] for example by using a relatively thick diffusive layer or under suitable hydrodynamic conditions (e.g. ≥200 rpm stirring rate in this study).[22]

The effect of the DBL on 11 test chemicals for DGT measurement was tested under simulated hydrodynamic conditions (**Figure S9**). Under the quiescent condition (stirring rate = 0 rpm), the calculated thickness of DBL was 520 μm using Equation (1.1), and the C_{DGT} of test chemicals would be only about 66% of the bulk concentrations of solution if calculated by Equation (1.2) (i.e. >30% underestimation). This effect of DBL on C_{DGT} underestimation was similar with the effect of

hydrodynamic condition on R_S measurement from most previous POCIS studies on POCs under quiescent batch experiments,[18, 19, 43] but much less than some results of POCs from MacLeod *et al*'s study.[44] When the stirring rate was 100 rpm, similar with the hydrodynamic conditions of very low water flow, the estimated DBL thickness was 137 μm. No significant differences were observed between C_{DGT} and C_b when stirring rate was larger than 200 rpm, which meant the thickness of DBL was so small that it could be negligible compared to the diffusion layer (this is why the stirring rate was set at 350 rpm for all the experiments in this study except the test of DBL effect, to make sure the DBL could be negligible). Therefore, the DGT measurement will not be significantly affected under normal water flow conditions. This is an appreciable advantage of DGT for most *in-situ* deployment situations, since the error on measurement using Equation (1.2) could be negligible (<<10%).[23, 24] This greatly simplifies field measurements, as there is no need to measure the DBL thickness.

3.7 Time and Diffusion Layer Thickness Dependence

The experiments of DGT time dependence and diffusion layer thickness dependence are important for confirming the validity of the DGT principle for the test chemicals. The test chemical concentrations in the solution did not change significantly during the whole deployment period (<5%). The 5-d experiment (**Figures 3a-b and S10**) showed that the DGT can simultaneously and continuously accumulate test chemicals and the accumulated test chemical amounts increased linearly (R^2 ranged from 0.9853 to 0.9995, p<0.001) with the deployment time, which agreed well with the theoretical prediction according to Equation (1.2). The ratios of C_{DGT}/ C_b were from 0.99±0.06 (E1) to 1.07±0.07 (MEP). The result indicates that HLB-DGT can be used for measuring the selected test chemicals in solution directly and

accurately.

According to the principles of DGT, the test chemical accumulation on the resin gels should be inversely proportional to the diffusion layer thickness, when DGT devices were exposed to a well-stirred solution of test chemicals for a fixed duration. Data for PRP and BPA are shown in **Figures 3c-d** as examples (all test chemicals data given in **Figure S11**) and agreed well with the theoretical prediction. The results also demonstrate that the DBL effect can be ignored when test solutions were well-stirred. The good fits of measured mass to predicted line confirm the use of appropriate diffusion coefficients in water. The results on both time and diffusion layer thickness dependence further confirm the DGT theory and mechanism, and validate the direct use of DGT for simultaneous measurements of 11 test chemicals in solutions.

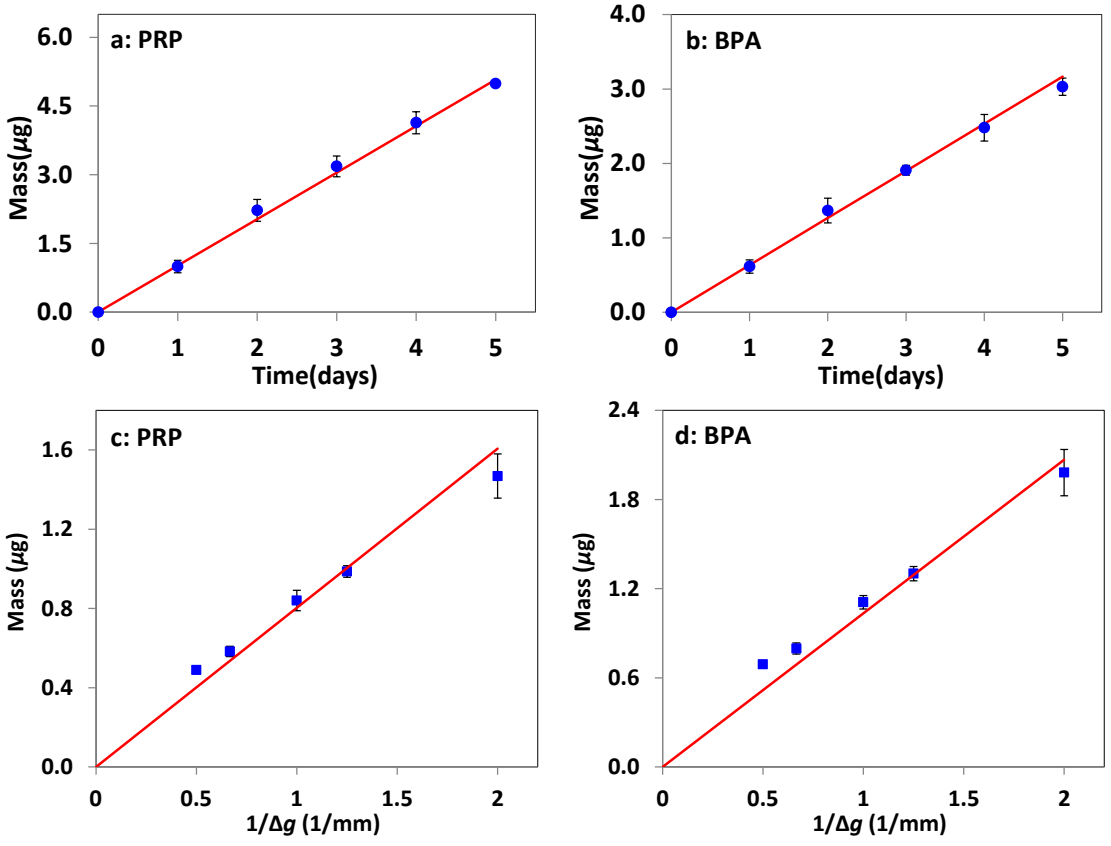


Figure 3: Measured masses (M, μg) of selected test chemicals in HLB-DGT deployed in well stirred solution for different time (a-b, n=3) and with various diffusion layer thicknesses (c-d, n=3). The solid lines are theoretical lines

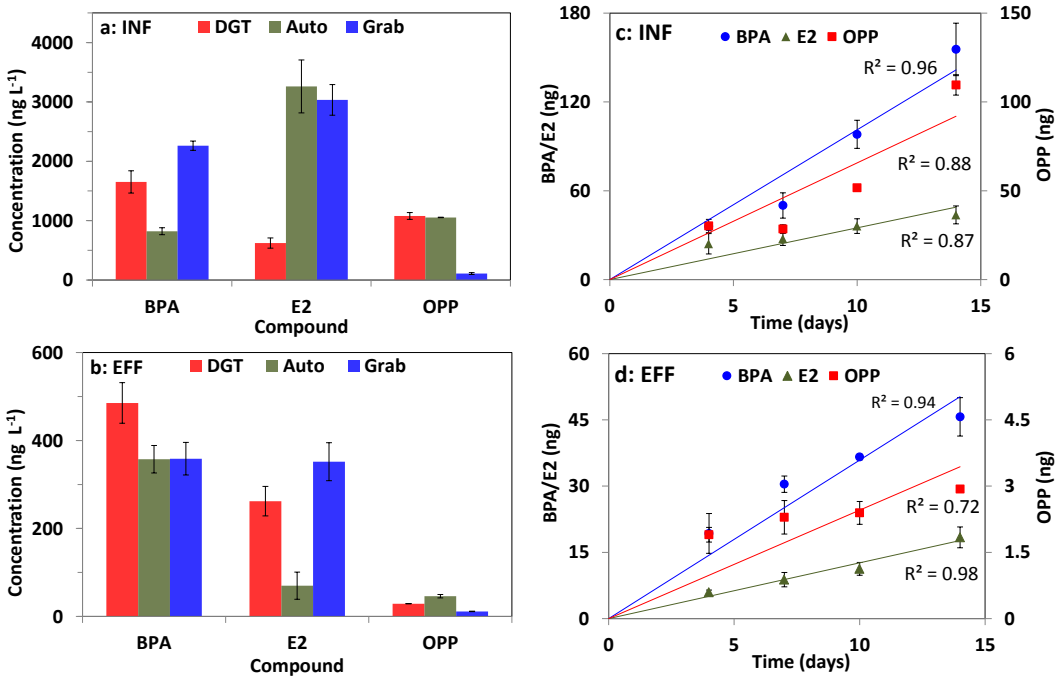
predicted by equation (1.2). Error bars: 1 SD.

3.8 Field Trial Application

To validate the application of DGT for measuring TWA concentrations of the selected test chemicals in waters, a series of DGT devices were deployed in a domestic WWTP in the UK (equipped with traditional activated sludge treatment process and the service population is ca. 100 000). The results given in **Figures 4** and **S12** showed that all 11 test chemicals, except IPRP, were detected in the influent for both active and DGT sampling methods. Apart from IPRP and PRP, all other test chemicals were found in the effluent. No test chemicals were detected from the blank DGT samples. For most of the detected test chemicals in DGT, the accumulated mass increases linearly with deployment time for 14 d in both the influent and effluent (**Figures 4** and **S12**, except E1 and E3 in the influent). This confirms that the DGT sampler is capable for measuring these test chemicals quantitatively in field conditions.

The 14-d TWA concentration of BPA, E2 and OPP sampled by DGT were calculated and presented in **Figure 4** as examples (full data set in **Table S7**). Significant, but non-systematic differences can be observed between *in situ* DGT measurements and measurements made from samples obtained by other methods. Similar results were found when HLB-POCIS was used for sampling pharmaceuticals in seawater[47] and for sampling EDCs in river water and wastewater,[42] and DGT used for sampling 4-CP in wastewater.[29] The major reasons for these differences probably include: i) DGT accumulated the dissolved fraction of test chemicals (nm range due to the diffusive gel pore size), but grab/auto samples contained some particulate fraction through filters (0.7 μm) which leads to higher concentrations in some cases and ii) lack of representative grab/auto samples (only 3 times samples) could be another reason leading to the differences among the three sampling methods, while DGT accumulated test chemicals

420 throughout the period, providing the TWA-concentration.



421

422 **Figure 4:** 14-day average concentrations of BPA, E2 and OPP for both active (grab/auto, n = 6) and HLB-DGT (n =
423 3) samples in the influent (a) and effluent (b), and HLB-DGT uptake of BPA, E2 and OPP in influent (c) and effluent
424 (d) for 14 days. Error bar: 1SD.

425

426 This DGT sampler could provide similar sampling rates per unit area ($R_{S/A}$) to other passive samplers,
427 such as POCIS and Chemcatcher. Although the total sampling rate of DGT is smaller, it can detect ng L^{-1}
428 concentration levels of 11 test chemicals in the aquatic environment when deployed for 7 days. Field tests
429 showed that the DGT device could sensitively detect the majority of test chemicals in 4 or 7 days. The
430 lower detection limits of DGT samplers and shorter deployment period could be achieved by a
431 combination of samples from parallel deployment of several DGT devices. This study has demonstrated
432 DGT theory for *in situ* measurement of several groups of organic chemicals. DGT samplers could be
433 developed by the selection of more suitable protective filters, diffusive layers and binding agents. We

recommend DGT samplers continue to be developed and tested for other groups of emerging organic chemicals.

SUPPORTING INFORMATION

Information including chemical standards, reagents, experiment control, analytical method, supplementary tables and figures was listed in the Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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Supporting Information for

Development of DGT passive sampling technique for *in situ* measurements of trace organic chemicals discharged in household wastewater

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Supplementary Figures

Figure S1: Ratio of test chemical concentrations in solution after (C_m) and before (C_w) deployment of DGT holder, PA gel (polyacrylamide diffusive gel), AG gel (agarose diffusive gel), PES filter (polyethenesulfone membrane, Pall, 0.45 μm), PC1 filter (cyclopore track etched membrane, Whatman, 0.2 μm), PC2 filter (track-etch membrane, Nuclepore Whatman, 0.2 μm), PC3 filter (polycarbonate membrane, Nuclepore, 0.015 μm) and CNM filter (cellulose nitrate membrane, Wuhtman, 0.2 μm; n=3). Error bars were calculated from the standard deviation (SD) of three replicates. Solid line (100 %) indicated no adsorption of test chemicals after deployment.

Figure S2: test chemical recoveries of HLB gels using ultrasonic extraction with 5 mL ACN for different time (15 min and 30 min) and numbers of extraction times (once and twice; n = 3). Error bars: 1 SD. Red solid lines indicated that the good recoveries for most compounds, which were between 60 % and 120 %.

Figure S3: Masses (μg) of test chemicals untaken by HLB resin gels in 50 mL test chemical solutions of various concentration at pH=6 and 8 (IS= 0.01M, T= 20 ± 2 ℃; n=3). Error bars: 1SD.

Figure S4: Dynamic binding of test chemicals by HLB resin gels in 20 mL solutions of 200 μg L^{-1} test chemicals (IS = 0.01 M and pH = 6.8 ± 0.1, T = 20 ± 2 ℃; n=3); Error bars: 1SD.

Figure S5: Masses of test chemicals diffused through agarose gel at different time in the diffusion cell (IS=0.01 M, pH=6.8 ± 0.1 and T= 25 ± 0.5 ℃).

Figure S6: Effect of pH on HLB-DGT measurement (IS = 0.01 M, T = 20 ± 2 ℃; n = 3). C_{DGT} are the test chemical concentrations measured by DGT and C_b, their concentrations in the bulk solutions. The solid horizontal lines represent the value of 1 and the dotted horizontal lines represent the values at 0.9 and 1.1. Error bars: 1SD.

Figure S7: Effect of IS on HLB-DGT performance (pH = 6.9 ± 0.2, T = 20 ± 2 ℃; n = 3). C_{DGT} are the test chemical concentrations measured by DGT and C_b, their concentrations in the bulk solutions. The solid horizontal lines represent the value of 1 and the dotted horizontal lines represent the values at 0.9 and 1.1. Error bars: 1SD.

Figure S8: Effect of DOM on HLB-DGT measurement (pH = 6.9 ± 0.2, IS = 0.01 M, T = 20 ± 2 ℃; n = 3). C_{DGT} are the test chemical concentrations measured by DGT and C_b, their concentrations in the bulk solutions. The solid horizontal lines represent the value of 1 and the dotted horizontal lines represent the values at 0.9 and 1.1. Error bars: 1SD.

Figure S9: Effect of stirring rate on HLB-DGT measurement (IS = 0.01 M, pH = 6.5 ± 0.1 T = 23 ± 2 ℃; n=3). C_{DGT} are the test chemical concentrations measured by DGT and C_b, their concentrations in the bulk solutions. The solid horizontal lines represent the value of 1. Error bars: 1SD.

Figure S10: Measured masses (M, μg) of test chemicals in HLB-DGT deployed in well stirred solution for different time (IS = 0.01 M, pH = 6.8 ± 0.2, T= 24 ± 2 ℃; n=3). The solid lines are theoretical lines predicted by equation (1). Error bars: 1 SD.

Figure S11: Measured masses (M, μg) of test chemicals accumulated in HLB-DGT deployed in well stirred solution with various diffusion layer thicknesses (IS = 0.01 M, pH = 6.8 ± 0.2, T = 24 ± 2 ℃; n=3). The solid lines are theoretical lines predicted by equation (1). Error bars: 1 SD.

Figure S12: Typical test chemicals uptake in DGT (right axis, n = 3) and water concentrations (C_w, left axis, Auto, auto sampling, n = 2; Grab, grab sampling, n = 2) of effluent and influent of a UK WWTP for 14 days. Error bar: 1SD.

Chemicals and Reagents

Reagents are at least analytical grade and ≥ 99% purity, organic solvents are HPLC grade. Sodium chloride (NaCl), sodium acetate (NaAc), sodium azide (NaN_3) and sodium bicarbonate ($NaHCO_3$) were also purchased from Sigma-Aldrich (UK). Hydrochloric acid (HCl, 35.5-37.5 %), sodium hydroxide (NaOH), ammonium acetate (NH_4Ac), methanol (MeOH) and acetonitrile (ACN) were obtained from Fisher Scientific (UK). Water used in the experiments was supplied from a Milli-Q water (MQ water) purification system (>18.2 MΩ/cm, Millipore, UK).

The reagents for gel making: gel solution was prepared and provided by DGT Research Ltd (UK), ammonium persulfate (APS) and N,N,N′,N′-Tetramethylethylenediamine (TEMED) were purchased from Sigma-Aldrich (UK) and agarose was obtained from Bio-Rad Laboratories (UK).

Lab experiment control description

New plastic-ware (including the DGT holders, water containers) was used for all experiments. It was immersed and soaked in the methanol overnight and rinsed thoroughly in MQ water before use. All glassware was fully immersed and soaked in the Decon 90 solution (4 %) overnight and then rinsed thoroughly with tap water and MQ water, followed by baking at 450 ℃ for 4 hours (h) before use.

During the lab experiments, the water solution pH was monitored both before and after the experiment (if the experiment time was less than 24 h) or daily (if the experiment time were more than 24 h) by a pH meter equipped with an Activon pH electrode (Radiometer Copenhagen, PHM93) to confirm the pH of water solution did not change more than 0.2 as adjusted, and the water temperature was measured every 8 h using a mercurial thermometer to ensure the temperature change was stayed within 2 ℃ as set. Solution pH was modified using NaAc and HCl for acidity or $NaHCO_3$ and NaOH for basicity. Ionic strength (IS) of the solution was adjusted using NaCl. Dissolved organic matter (DOM) concentration was changed by adding humic acid solution in the water solution. All experiments were undertaken in a cool and dark room and the water containers were covered by aluminium foil to prevent possible photo-degradation of test chemicals during the deployment period, 0.02% of NaN_3 was added into the solution to repress the microbial activities and bio-degradation. During the period of experiments, 0.4 mL of tested water solution was sampled at the beginning, middle (or daily when taking the DGT devices out) and end of the experiments to check for possible concentration changes in solution (similar sampling procedures were undertaken for all experiments unless stated specially). Blank and control experiments were conducted in every set of the experiments to prevent the possible contamination/change during the experiment, such as the degradation and adsorption to the tested materials or on the container wall/DGT devices.

All the laboratory experiments and field sampling were carried out at least in triplicate unless stated specifically, and the results were expressed as the average ± standard deviation (SD). The statistical analysis was conducted by IBM SPSS Statistics software (Version 22), the significant differences were statistically tested by analysis of variance (ANOVA) at 5 % significant level.

Analytical method

Field sample preparation

Test chemicals in DGT samples were extracted according to the optimised procedure. Briefly, once retrieved, the DGT holders were rinsed with MQ water thoroughly before disassembly. The filter and diffusive gel layer were peeled off, and the resin gel layer was placed in a clean baked amber sample vial. 5 mL of ACN was added to the vial to extract the test chemicals from the resin gel. 100 ng of internal standards (^{13}C MEP, ^{13}C PRP, BPA-d16, E1-d4, E2-d5, BHA-d3, ^{13}C OPP and TCS-d3) was added before extraction. The vials were placed into an ultrasonic bath for 30 minutes to extract.

The water samples were transported to the lab after collection and stored in the dark room at 4 ℃ and treated in 24 h. The pre-treatment of wastewater was conducted according to a published procedure[1, 2] with minor modification. In brief, water samples were filtered (Whatman GF/F filter, 0.7 μm) to remove suspended particles. 500 mL sample was used for solid-phase extraction (SPE) using an HLB cartridge (200 mg, 6 mL, Sigma-Aldrich, UK). 100 ng of internal standards (^{13}C MEP, ^{13}C PRP, BPA-d16, E1-d4, E2-d5, BHA-d3, ^{13}C OPP and TCS-d3) was added into filtered samples before extraction. The SPE cartridge was preconditioned with 10ml MeOH followed by 10 ml MQ water. The water samples were then introduced into the cartridge at a flow rate of 5 mL min^{-1}. After the water sample passage, the sample bottle was rinsed twice with two aliquots of 50 mL of 5 % (v/v) methanol in MQ water, which passed through the cartridge. After loading, the cartridges were rinsed with 10 mL MQ water and vacuum dried for 30 min. The test chemicals held on cartridges were eluted with 10 mL MeOH.

Both DGT and wastewater sample extracts were then blown to about 1 mL under a gentle flow of N_2, followed by syringe filtering (0.22 μm) to amber vials, stored at -20 ℃ waiting for liquid chromatography- mass spectrometer (LC-MS) analysis. Just prior to the LC-MS analysis, 200 μL aliquot of each water sample extract (300 μL of DGT samples) were dried under a gentle N_2 flow and reconstituted in 100 μL (50 μL of DGT samples) of water and methanol mixture with 5mM NH_4OH (50 % : 50 %, v/v).

HPLC for lab experiment samples

A Thermo Finnigan high performance liquid chromatography (HLPC) coupled with a photodiode array

153 detector (DAD) was employed to analyse the 11 target chemicals at the maximum ultraviolet (UV) absorbance
154 of 260 nm and 280 nm. An Agilent C8 (150 mm × 2.1 mm, 5 μm) LC column was used to separate the
155 chemicals. The mobile phases were A: MQ water (0.01 % NaN_3 added) and B: acetonitrile (ACN). The
156 gradient procedure was optimised: the gradient began at 20 % B (equilibrium time 0.5 min), then increased to
157 71.5 % B within 23.3 min and then increased to 100 % B in 1 min, held for 5 min, after that decreased to the
158 initial condition (20 % B) in 1 min, finally, a post-run time of 10 min ensured re- equilibrium of the column
159 before the next injection. The injection volume of samples (composition of sample was 50 % water : 50 %
160 MeOH for water samples, and 50 % water : 50 % ACN for DGT samples) was 10 μL and the column and the
161 tray temperature were kept at 25 ℃. External standard method was used to quantify the target chemicals, and
162 the test chemicals were identified on the basis of the retention time. A six-point response calibration was
163 established to quantify the target analyses. The instrument limits of detection (IDLs) calculated based on the 3
164 times of ratios of signal/noise (S/N >3) were ranged from 1.16 to 2.35 $\mu g\ L^{-1}$.

165 **LC-MS for field samples**

166 The 11 test chemicals were separated by a Waters Xbridge C18 column (2.5 μm, 2.1 × 100mm) on an Agilent
167 1100 HPLC system. An Agilent 6100 single quadrupole mass spectrometer equipped with an electrospray
168 ionisation source was used to analyse both wastewater and DGT samples in negative mode.
169 The LC setting for field sample analysis (including the temperature, gradient procedure and injection volume)
170 was as above except the pure MQ water was changed to MQ water with 5 mM NH_4OH to enhance the
171 response of compounds in negative scan. The MS parameters including drying gas flow and temperature,
172 nebulizer pressure, capillary voltage and fragmentor were optimised using flow injection analysis without a
173 column for the best response of target ions of chemicals. LC-MS was optimally operated in negative ion mode
174 with a capillary voltage of 2.5 kV, a dry gas temperature of 350 ℃, a drying gas flow of 10 L $h^{-1}$and a
175 nebulizer pressure of 30 psi. The optimised fragmentor was shown in **Table S0**. Selected ion monitoring
176 (SIM) mode was used to detect the compounds. The target compounds were identified based on both retention
177 time and target ions. A nine-point response calibration ranged from 1 to 400 $\mu g\ L^{-1}$ was established to quantify
178 the target analytes. The method detection limits (MDLs) for the field samples are showed in **Table S2**.

Table S0: LC-MS parameters for test chemicals.

Chemical	Ion	Fragmentor (V)
MEP	151	80
^{13}C MEP	157	80
E3	287	140
IPRP	179	100
PRP	179	100
^{13}C PRP	185	100
BPA	227	120
BPA-d16	241	100
E2	271	140
E2-d5	276	140
EE2	295	160
OPP	169	100
^{13}C OPP	175	100
E1	269	140
E1-d4	273	140
BHA	179	80
BHA-d3	182	80
TCS	287/289	80
TCS-d3	290/292	80

183 **Table S1:** Purity of standards and physical-chemical properties of 11 test chemicals.

184

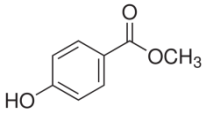
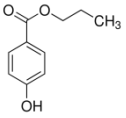
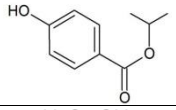
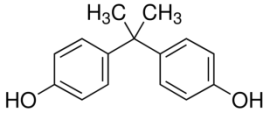
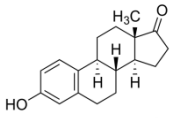
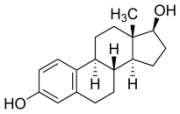
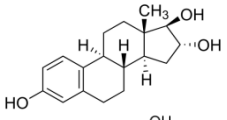
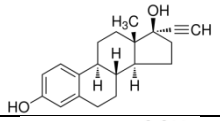
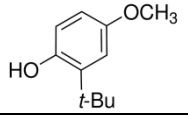
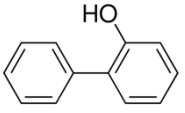
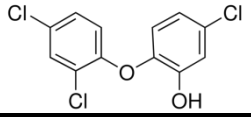
Group	Chemical and purity	Abbr.	CAS No.	Molecular formula	Molecular weight	Sw (mg/L)	pKa	$LogK_{OW}$	Structure
Preservative	Methylparaben ≥99.0 %	MEP	99-76-3	$C_8H_8O_3$	152.15	2500	8.31	2	
	Propylparaben ≥99.0 %	PRP	94-13-3	$C_{10}H_{12}O_3$	180.2	500	8.23	2.98	
	Isopropylparaben ≥99.0 %	IPRP	4191-73-5	$C_{10}H_{12}O_3$	180.2	689.7	8.4	2.91	
Estrogen	Bisphenol-A ≥99.0 %	BPA	1980-5-7	$C_{15}H_{16}O_2$	228.29	120	9.94/ 11.97	3.64	
	Estrone ≥99.0 %	E1	53-16-7	$C_{18}H_{22}O_2$	270.37	30	10.33	3.43	
	β-Estradiol ≥98.0 %	E2	50-28-2	$C_{18}H_{24}O_2$	272.39	3.9	10.33	3.94	
	Estriol ≥99.0 %	E3	50-27-1	$C_{18}H_{24}O_3$	288.39	440.8	10.33/ 13.62	2.81	
	17*α*-Ethinylestradiol ≥98.0 %	EE2	57-63-6	$C_{20}H_{24}O_2$	296.41	11.3	10.33	4.12	
Antioxidant	Butylated hydroxyanisole ≥98.5 %	BHA	1948-33-0	$C_{11}H_{16}O_2$	180.24	212.8	10.55	3.5	
Disinfectant	Ortho-phenylphenol ≥99.0%	OPP	90-43-7	$C_{12}H_{10}O$	170.21	700	9.65	3.28	
	Triclosan ≥97%	TCS	3380-34-5	$C_{12}H_7Cl_3O_2$	289.55	10	7.68	4.66	

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Table S2: Recoveries of test chemicals for SPE and DGT and detection limits (IDLs and MDLs) for both water and DGT samples during the lab experiments detected by LC-DAD and field application detected by LC-MS.

Compound	IDL ng ml^{-1}		Recoveries, % (average ± SD) n=3		D_e at 25 °C[a] cm^2 s^{-1}	MDL [b] for the lab samples, ng mL^{-1}		MDL for the field samples, ng L^{-1}	
	LC-DAD	LC-MS	SPE	DGT		Water	DGT [c]	Water	DGT
MEP	1.16	0.48	91.9 ± 4.9	122 ± 5.6	6.85E-6	2.32	0.52	0.52	0.51
IPRP	1.43	0.32	81.3 ± 4.9	122 ± 10.8	5.92E-6	2.86	0.74	0.35	0.39
PRP	1.64	0.37	82.5 ± 5.7	123 ± 11.1	5.91E-6	3.28	0.84	0.41	0.45
E1	2.17	2.54	89.7 ± 1.8	72.2 ± 8.3	4.80E-6	4.34	2.33	2.76	6.49
E2	2.04	3.65	83.5 ± 1.9	87.6 ± 7.5	3.58E-6	4.08	2.42	3.98	10.3
E3	1.82	2.37	85.2 ± 11.0	103 ± 12.4	4.59E-6	3.64	1.43	2.58	4.44
EE2	2.35	4.03	83.2 ± 7.4	112 ± 18.3	3.40E-6	4.70	2.29	4.38	9.35
BPA	1.79	0.77	82.6 ± 1.8	102 ± 6.2	4.80E-6	3.58	1.36	0.84	1.39
BHA	1.87	1.56	61.3 ± 9.7	64.6 ± 5.0	4.25E-6	3.74	2.54	1.79	5.31
OPP	1.55	2.99	77.3 ± 2.5	96.1 ± 5.3	5.18E-6	3.10	1.16	3.26	5.33
TCS	1.91	0.87	84.1 ± 8.2	87.9 ± 11.6	3.63E-6	3.82	2.23	0.95	2.41

a D_e: The De values were selected from **Table S4**;

b MDLs: calculated using the equation: $\mathrm{MDL} = \frac{\mathrm{IDL}}{\mathrm{R} \times \mathrm{CF}}$, [3] where R is the absolute recovery for water or DGT samples and the CF is the concentration factor;

c DGT MDLs (ng ml^{-1} or ng L^{-1}): calculated based on the DGT MDLs (ng per DGT) for 1-day deployment in the lab experiments and 7-day deployment in the field application under 25 °C condition.

Table S3: Overall recoveries (%) and separate recoveries (%) of test chemical extraction for HLB resin gels at 100, 250 and 500 μg L^{-1} solution (n=4 for each concentration, n=12 in total).

Gel		MEP	E3	IPRP	PRP	BPA	E2	EE2	OPP	E1	BHA	TCS
Overall	Average	122	103	123	122	102	87.6	112	96.1	72.2	64.6	87.9
	SD	5.6	12.4	11.1	10.8	6.2	7.5	18.3	5.3	8.3	5.0	11.6
100 μg L^{-1}	Average	122	117	122	116	100	80.4	136	96.1	81.1	62.1	98.7
	SD	2.8	5.6	20.4	16.8	2.1	2.9	8.6	6.1	6.7	4.6	6.9
250 μg L^{-1}	Average	125	101	122	129	110	94.0	101	99.7	70.6	66.0	90.8
	SD	8.4	7.5	3.4	4.3	4.0	7.9	3.8	5.4	3.9	7.3	5.0
500 μg L^{-1}	Average	117	90.9	126	122	97.3	88.4	99.6	92.4	64.9	65.7	74.3
	SD	1.7	3.2	2.7	5.1	3.4	3.3	4.3	1.5	3.0	2.7	2.6

198 **Table S4:** Estimated capacities of three resin gels (μg/gel) and maximum water concentrations for typical

199 deployment time.

200

	HLB		C_b (μg L^{-1})	
	pH=6	pH=8	2 weeks	1 month
MEP	22.8	11.8	45.50	21.24
PRP	66.4	63.4	119.18	55.62
IPRP	42.5	47.4	189.41	88.39
BPA	77.8	79.4	282.05	131.62
E1	60.5	53.6	426.81	199.18
E2	58.1	54.0	397.29	185.40
E3	20.9	20.8	1095.63	511.29
EE2	141.5	143.6	339.91	158.62
BHA	53.0	62.1	294.00	137.20
OPP	78.3	66.9	328.55	153.32
TCS	110.6	97.0	703.29	328.20

201
202

Table S5: Diffusion coefficients (D_e) for 11 test chemicals at temperatures from 1 to 35 ℃ (E-06 cm^2 s^{-1}).

T (℃)	MEP	PRP	IPRP	E1	E2	E3	EE2	BPA	BHA	OPP	TCS
1	3.19	2.76	2.76	2.24	1.67	2.14	1.59	2.24	1.99	2.42	1.69
2	3.32	2.87	2.86	2.33	1.73	2.22	1.65	2.32	2.06	2.51	1.76
3	3.44	2.98	2.97	2.41	1.80	2.31	1.71	2.41	2.14	2.60	1.82
4	3.57	3.09	3.08	2.50	1.86	2.39	1.77	2.50	2.22	2.70	1.89
5	3.70	3.20	3.19	2.59	1.93	2.48	1.84	2.59	2.30	2.80	1.96
6	3.83	3.31	3.30	2.69	2.00	2.57	1.90	2.68	2.38	2.90	2.03
7	3.96	3.43	3.42	2.78	2.07	2.66	1.97	2.78	2.46	3.00	2.10
8	4.10	3.55	3.54	2.88	2.14	2.75	2.04	2.88	2.55	3.10	2.17
9	4.24	3.67	3.66	2.98	2.22	2.85	2.11	2.97	2.64	3.21	2.25
10	4.38	3.79	3.78	3.08	2.29	2.94	2.18	3.07	2.72	3.32	2.32
11	4.53	3.92	3.91	3.18	2.37	3.04	2.25	3.18	2.82	3.43	2.40
12	4.68	4.05	4.04	3.28	2.44	3.14	2.32	3.28	2.91	3.54	2.48
13	4.83	4.18	4.17	3.39	2.52	3.24	2.40	3.38	3.00	3.65	2.56
14	4.98	4.31	4.30	3.50	2.60	3.34	2.47	3.49	3.10	3.77	2.64
15	5.14	4.44	4.43	3.61	2.69	3.45	2.55	3.60	3.19	3.89	2.72
15*	**5.13**	**4.78**	**4.89**	**3.97**	**2.57**	**3.43**	**2.68**	**3.81**	**3.36**	**4.04**	**2.83**
16	5.30	4.58	4.57	3.72	2.77	3.55	2.63	3.71	3.29	4.01	2.81
17	5.46	4.72	4.71	3.83	2.85	3.66	2.71	3.83	3.39	4.13	2.89
18	5.62	4.86	4.85	3.95	2.94	3.77	2.79	3.94	3.49	4.25	2.98
19	5.79	5.01	4.99	4.06	3.03	3.88	2.87	4.06	3.60	4.38	3.07
20	5.96	5.15	5.14	4.18	3.11	4.00	2.96	4.18	3.70	4.51	3.16
20*	**6.23**	**5.31**	**5.24**	**4.35**	**3.29**	**3.83**	**3.26**	**4.08**	**3.41**	**4.69**	**3.35**
21	6.13	5.30	5.29	4.30	3.20	4.11	3.04	4.30	3.81	4.64	3.25
22	6.31	5.45	5.44	4.42	3.30	4.23	3.13	4.42	3.92	4.77	3.34
23	6.48	5.61	5.59	4.55	3.39	4.35	3.22	4.54	4.03	4.90	3.44
24	6.66	5.76	5.75	4.68	3.48	4.47	3.31	4.67	4.14	5.04	3.53
25*	**6.85**	**5.92**	**5.91**	**4.80**	**3.58**	**4.59**	**3.40**	**4.80**	**4.25**	**5.18**	**3.63**
26	7.03	6.08	6.07	4.93	3.68	4.72	3.49	4.93	4.37	5.32	3.73
27	7.22	6.24	6.23	5.07	3.77	4.84	3.59	5.06	4.49	5.46	3.83
28	7.41	6.41	6.39	5.20	3.87	4.97	3.68	5.20	4.61	5.60	3.93
29	7.60	6.58	6.56	5.34	3.97	5.10	3.78	5.33	4.73	5.75	4.03
30	7.80	6.75	6.73	5.47	4.08	5.23	3.87	5.47	4.85	5.90	4.14
31	8.00	6.92	6.90	5.61	4.18	5.37	3.97	5.61	4.97	6.05	4.24
32	8.20	7.09	7.08	5.75	4.29	5.50	4.07	5.75	5.10	6.20	4.35
33	8.40	7.27	7.25	5.90	4.39	5.64	4.17	5.89	5.22	6.36	4.46
34	8.61	7.45	7.43	6.04	4.50	5.78	4.28	6.04	5.35	6.51	4.57
35	8.82	7.63	7.61	6.19	4.61	5.92	4.38	6.18	5.48	6.67	4.68

* Measured diffusion coefficients

Table S6: Average ratios of C_{DGT}/C_b for HLB-DGTs under different pH (n=18), IS (n=12) and DOM (n=15) conditions.

Condition	Statistics	MEP	PRP	IPRP	E1	E2	E3	EE2	BPA	BHA	OPP	TCS
pH 3.5-9.5	Average	1.00	0.99	0.99	0.97	1.08	1.04	1.06	1.01	0.98	1.03	0.85
	SD	0.07	0.06	0.06	0.07	0.06	0.12	0.09	0.07	0.07	0.06	0.19
IS 0.001-0.5M	Average	0.97	0.95	0.97	0.98	0.98	1.02	1.01	0.99	0.93	0.94	0.76
	SD	0.08	0.10	0.06	0.06	0.07	0.05	0.07	0.12	0.10	0.17	0.11
DOM 0-20 mg/L	Average	1.03	1.01	1.00	1.00	1.09	0.99	1.13	1.06	0.97	1.05	0.74
	SD	0.03	0.04	0.04	0.05	0.05	0.05	0.06	0.04	0.04	0.05	0.03

Table S7: TWA-concentration of DGT and average concentration for active water samples (ng L^{-1}).

	Effluent					
	7 days deployment			14 days deployment		
	DGT	Grab-sample	Auto-sample	DGT	Grab-sample	Auto-sample
MEP	< MDL	0.59 ± 0.05	< MDL	< MDL	0.90 ± 0.33	0.77 ± 0.08
PRP	< MDL	< MDL	< MDL	< MDL	< MDL	< MDL
IPRP	< MDL	< MDL	< MDL	< MDL	< MDL	< MDL
BPA	646.76 ± 39.19	257.21 ± 22.11	429.42 ± 47.04	485.40 ± 46.23	358.57 ± 31.34	357.42 ± 37.02
E1	< MDL	10.32 ± 1.52	38.77 ± 6.13	6.49 ± 0.10	34.12 ± 2.98	39.78 ± 4.67
E2	250.92 ± 46.38	374.08 ± 35.24	49.17 ± 17.50	261.97 ± 33.53	351.76 ± 30.92	69.70 ± 43.14
E3	48.39 ± 18.51	< MDL	2311.54 ± 4.30	72.39 ± 1.82	< MDL	1735.69 ± 122.81
EE2	203.09 ± 39.46	4486.09 ± 96.83	4242.89 ± 397.08	203.30 ± 24.18	4667.81 ± 159.84	4149.99 ± 405.43
BHA	10.71 ± 1.63	684.46 ± 278.86	302.42 ± 144.47	7.19 ± 0.40	669.48 ± 325.83	339.67 ± 141.06
OPP	45.19 ± 7.46	11.51 ± 5.23	65.19 ± 0.29	28.87 ± 0.28	11.35 ± 3.85	45.89 ± 0.60
TCS	113.07 ± 39.58	666.05 ± 14.18	797.00 ± 8.35	105.53 ± 5.77	643.06 ± 14.34	726.57 ± 24.12
	Influent					
	7 days deployment			14 days deployment		
	DGT	Grab-sample	Auto-sample	DGT	Grab-sample	Auto-sample
MEP	310.62 ± 53.82	489.39 ± 2.52	200.56 ± 80.70	266.74 ± 15.13	467.75 ± 2.79	179.66 ± 85.41
PRP	89.22 ± 17.04	261.38 ± 1.27	200.27 ± 10.20	123.65 ± 20.08	229.08 ± 2.13	171.10 ± 26.61
IPRP	< MDL	< MDL	< MDL	< MDL	< MDL	< MDL
BPA	1063.94 ± 181.99	785.21 ± 28.38	668.69 ± 37.17	1652.81 ± 188.76	2263.28 ± 59.11	821.66 ± 78.76
E1	117.19 ± 19.08	544.43 ± 31.15	150.71 ± 8.65	135.62 ± 10.76	477.94 ± 47.62	117.12 ± 8.28
E2	784.22 ± 128.18	669.20 ± 45.46	3677.43 ± 197.19	622.35 ± 86.15	3035.73 ± 447.06	3262.21 ± 258.52
E3	257.57 ± 58.78	349.36 ± 62.14	154.07 ± 39.86	125.96 ± 20.24	531.03 ± 65.25	154.61 ± 30.28
EE2	1711.60 ± 241.17	17542.20 ± 2919.65	4562.66 ± 668.95	2279.91 ± 126.30	12534.08 ± 2082.10	4287.90 ± 506.57
BHA	12.62 ± 2.20	33.62 ± 7.56	37.09 ± 7.74	10.03 ± 1.10	59.19 ± 8.94	39.93 ± 5.80
OPP	559.58 ± 47.82	93.83 ± 3.64	1554.75 ± 6.21	1079.49 ± 56.87	108.45 ± 4.89	1053.74 ± 15.05
TCS	159.55 ± 11.44	887.67 ± 12.75	771.60 ± 18.33	283.00 ± 78.21	866.11 ± 9.16	781.54 ± 17.71

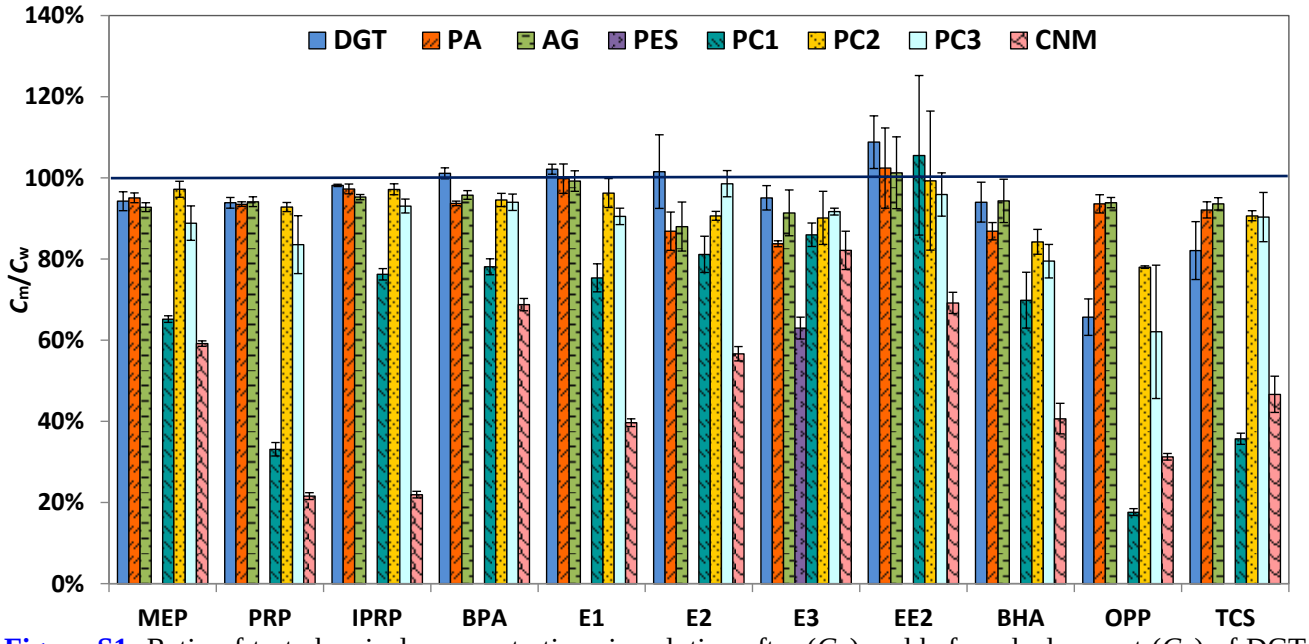
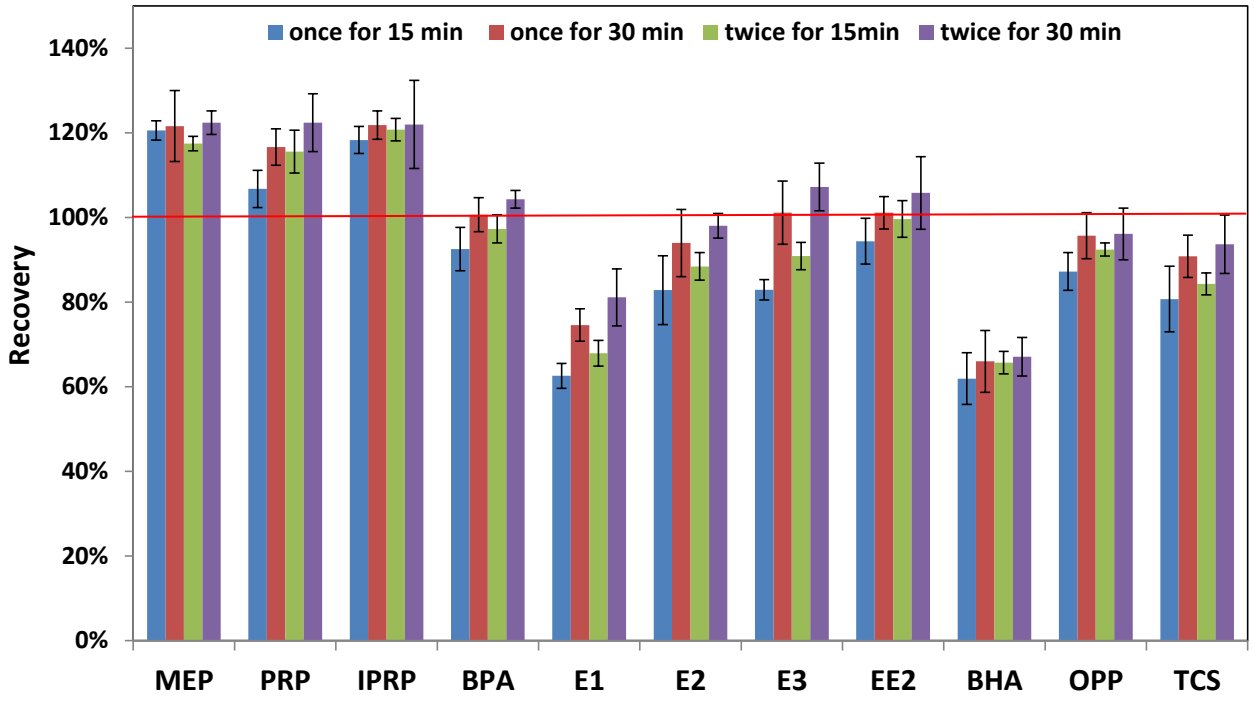
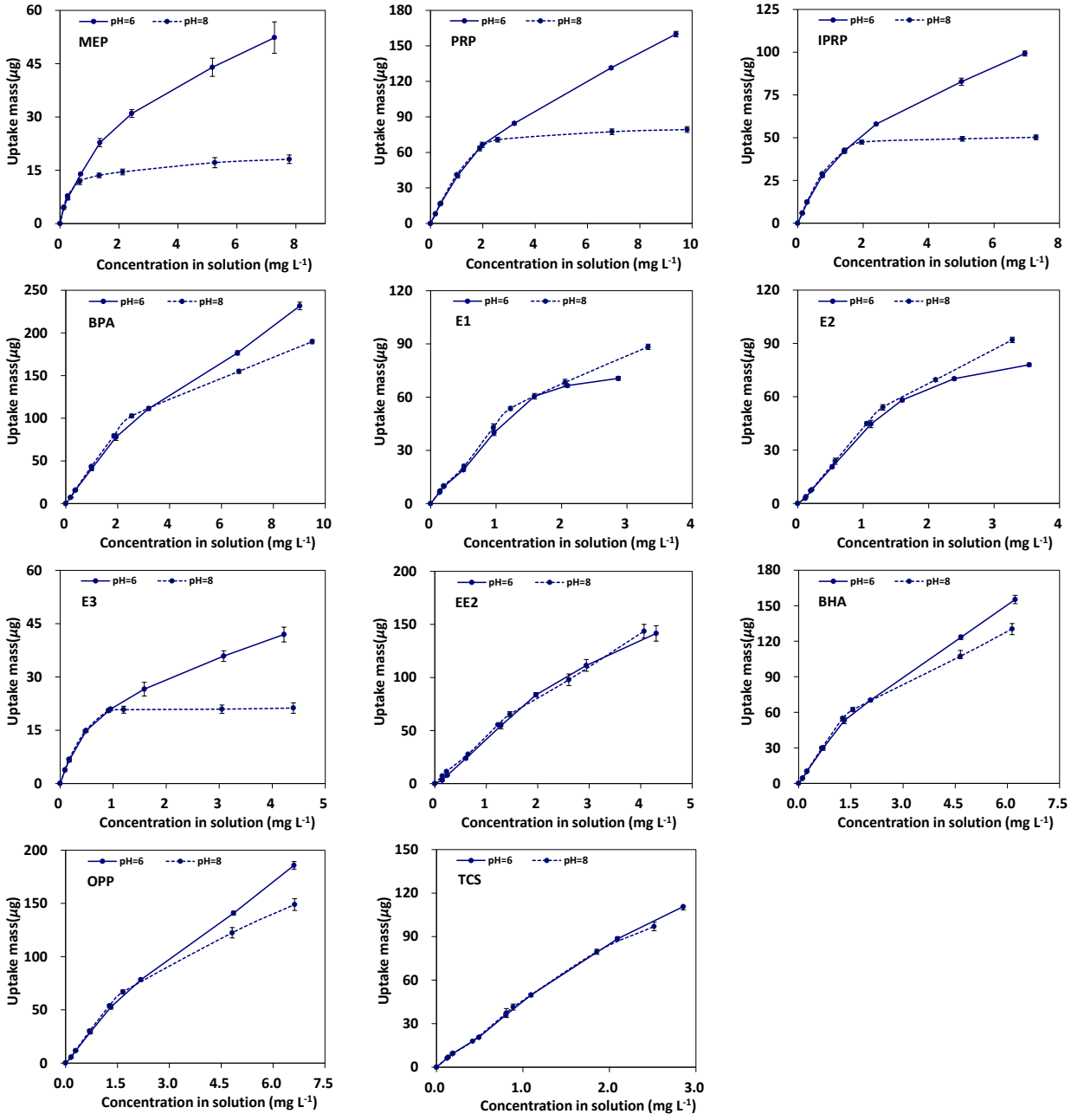


Figure S1: Ratio of test chemicals concentrations in solution after (C_m) and before deployment (C_w) of DGT holder, PA gel (polyacrylamide diffusive gel), AG gel (agarose diffusive gel), PES filter (polyethenesulfone membrane, Pall, 0.45 μm), PC1 filter (cyclopore track etched membrane, Whatman, 0.2 μm), PC2 filter (track-etch membrane, Nuclepore Whatman, 0.2 μm), PC3 filter (polycarbonate membrane, Nuclepore, 0.015 μm) and CNM filter (cellulose nitrate membrane, Whatman, 0.2 μm; n=3). Error bars were calculated from the standard deviation (SD) of three replicates. Solid line (100 %) indicates no adsorption of test chemicals after deployment.



223
224 **Figure S2:** Test chemical recoveries of HLB gels using ultrasonic extraction with 5 mL ACN for different
225 time (15 min and 30 min) and numbers of extraction times (once and twice; n = 3). Error bars: 1 SD. Red solid
226 lines indicated recovery of 100 %.

227



228
229 **Figure S3:** Masses (μg) of test chemical uptake by HLB resin gels in 50 mL test chemical solutions of various
230 concentration at pH=6 and 8 (IS= 0.01M, T= 20 ±2 ℃; n=3). Error bars: 1SD.

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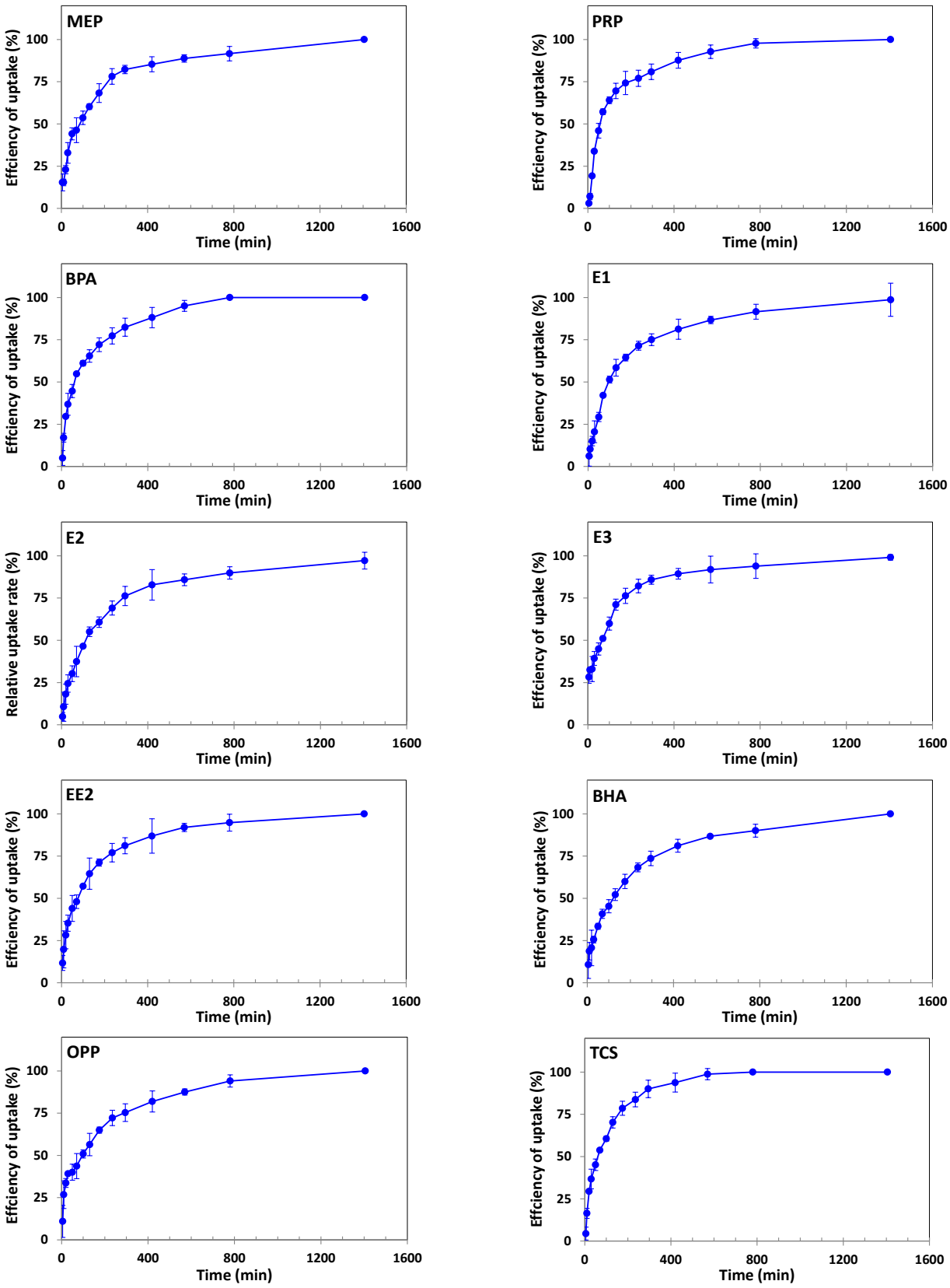

Figure S4: Dynamic binding of test chemicals by HLB resin gels in 20 mL solutions of 200 μg L^{-1} test chemicals (IS = 0.01 M and pH = 6.8 ±0.1, T = 20 ±2 ℃; n=3); Error bars: 1SD.

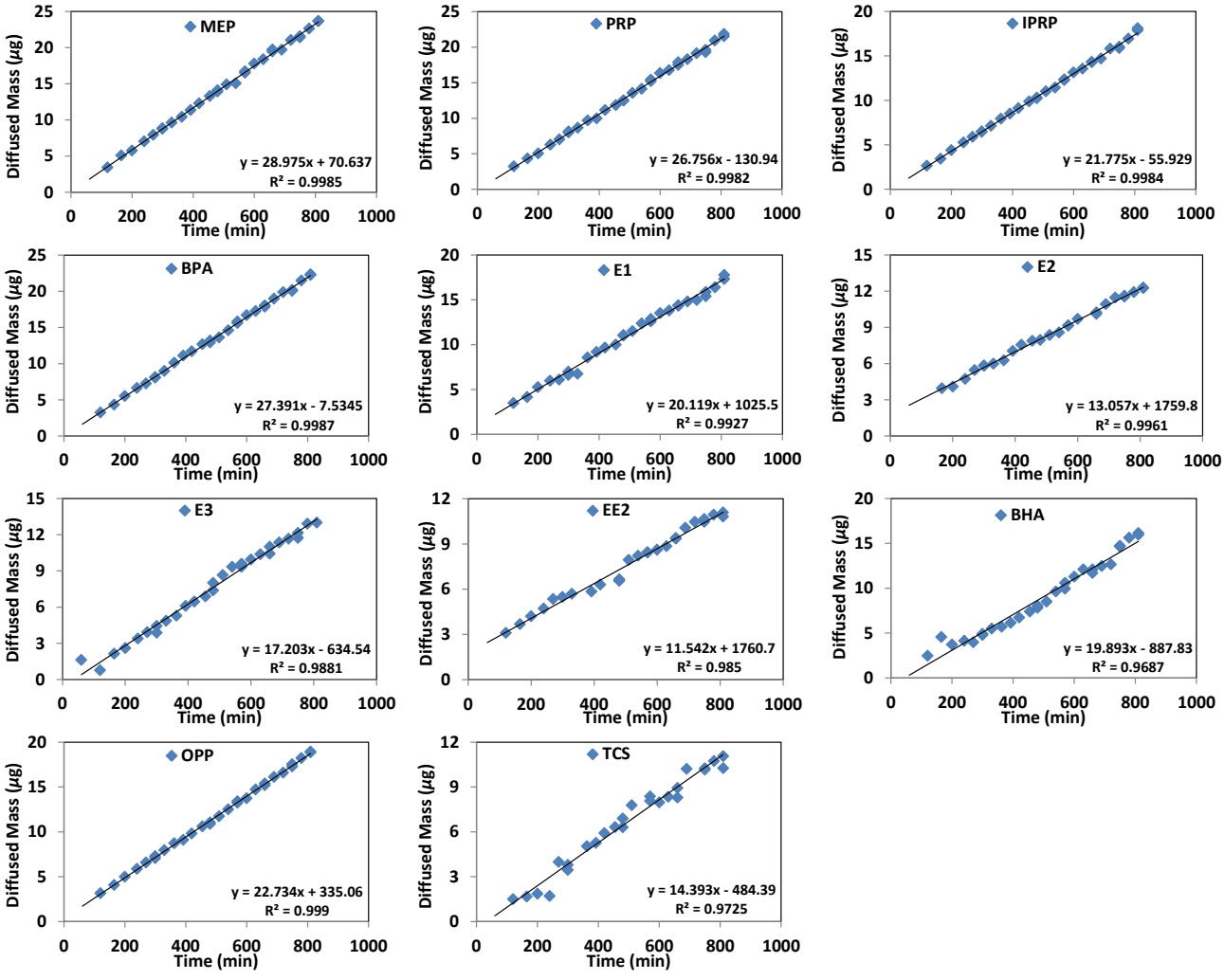

Figure S5: Masses of test chemicals diffused through agarose gel at different time in the diffusion cell (IS=0.01 M, pH=6.8 ±0.1 and *T*= 25 ±0.5 ℃).

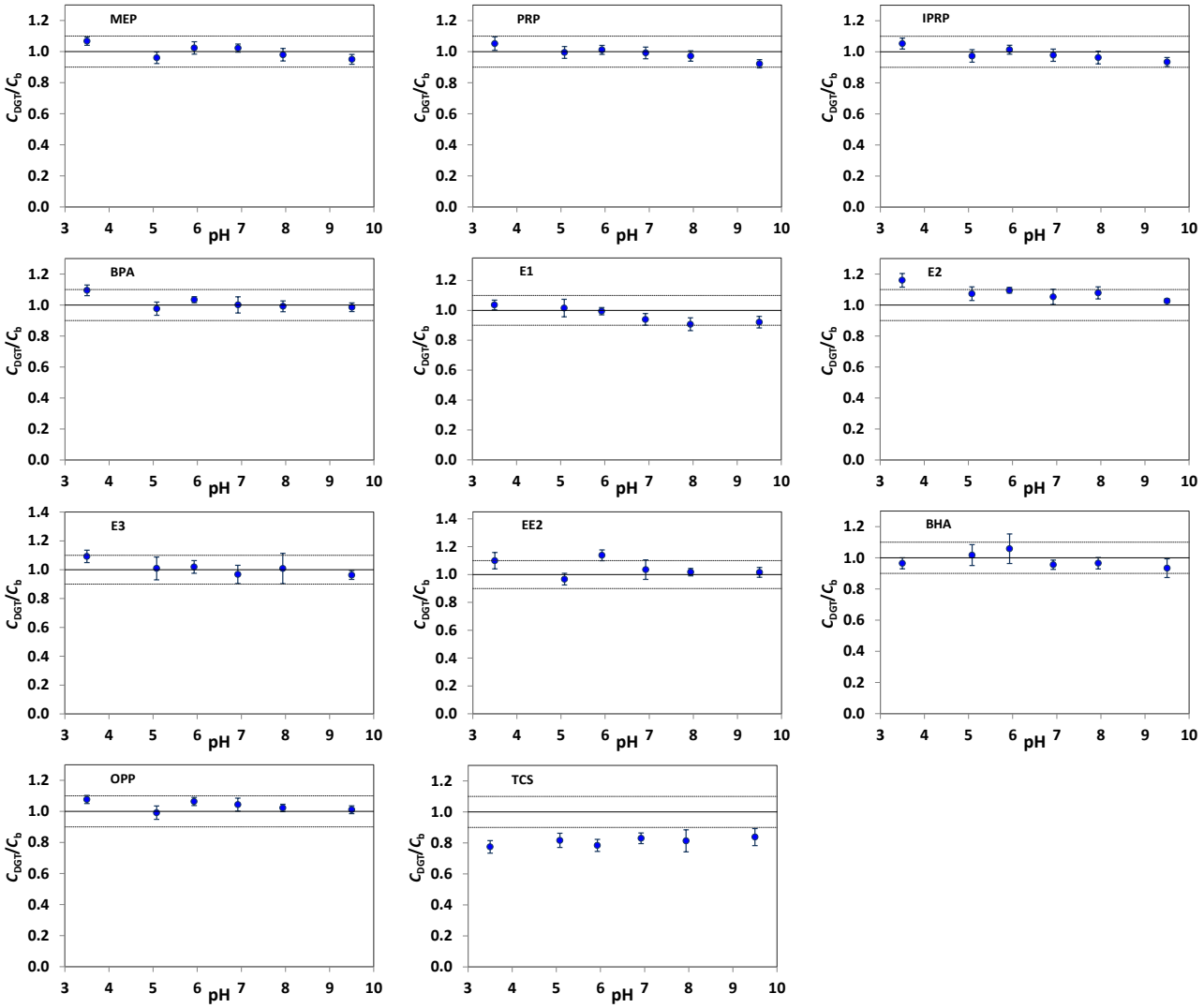

Figure S6: Effect of pH on HLB-DGT measurement (IS = 0.01 M, T = 20 ± 2 ℃; n = 3). C_{DGT} are the test chemical concentrations measured by DGT and C_b, their concentrations in the bulk solutions. The solid horizontal lines represent the value of 1 and the dotted horizontal lines represent the values at 0.9 and 1.1. Error bars: 1SD.

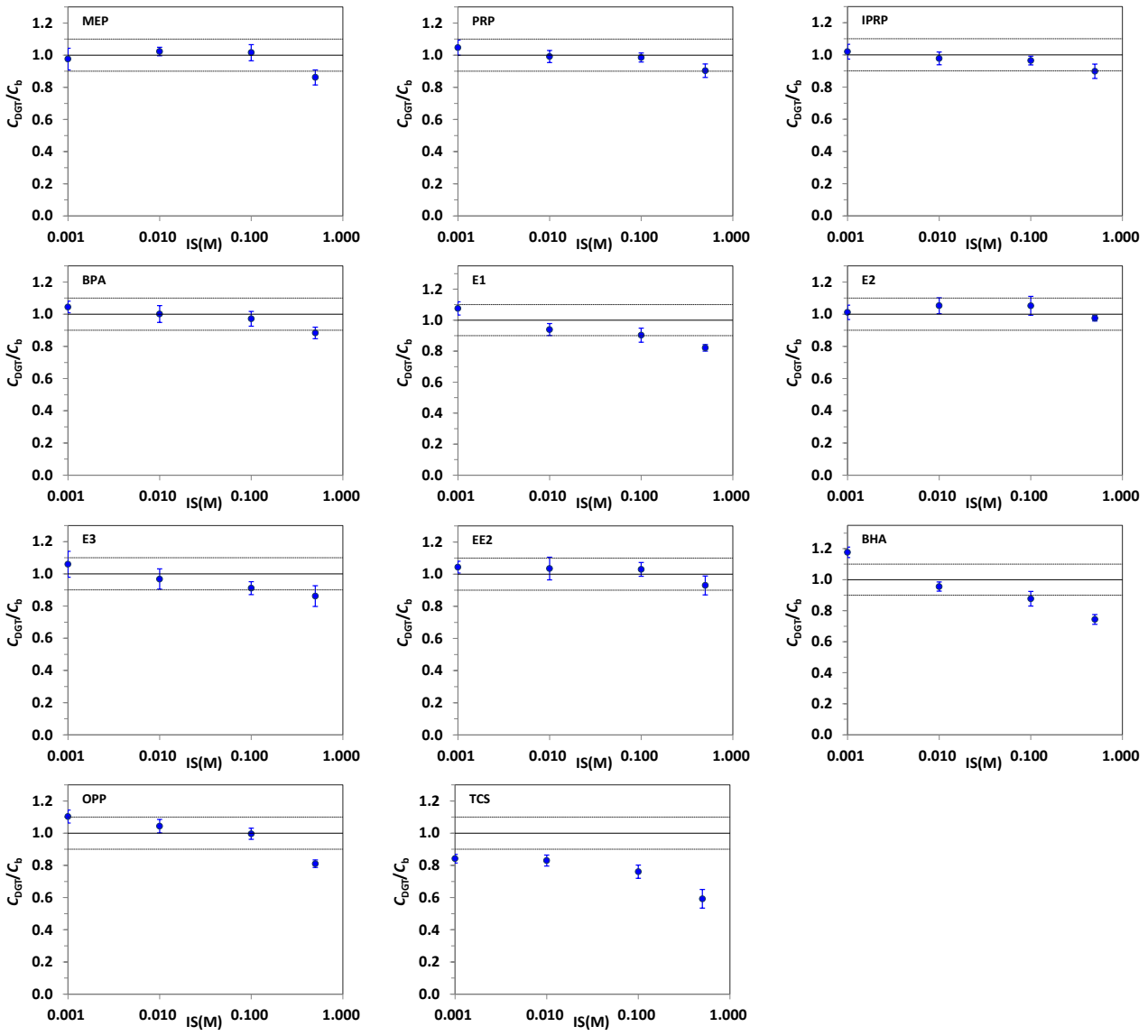

Figure S7: Effect of IS on HLB-DGT performance (pH = 6.9 ± 0.2, T = 20 ± 2 ℃; n = 3). C_{DGT} are the test chemical concentrations measured by DGT and C_b, their concentrations in the bulk solutions. The solid horizontal lines represent the value of 1 and the dotted horizontal lines represent the values at 0.9 and 1.1. Error bars: 1SD.

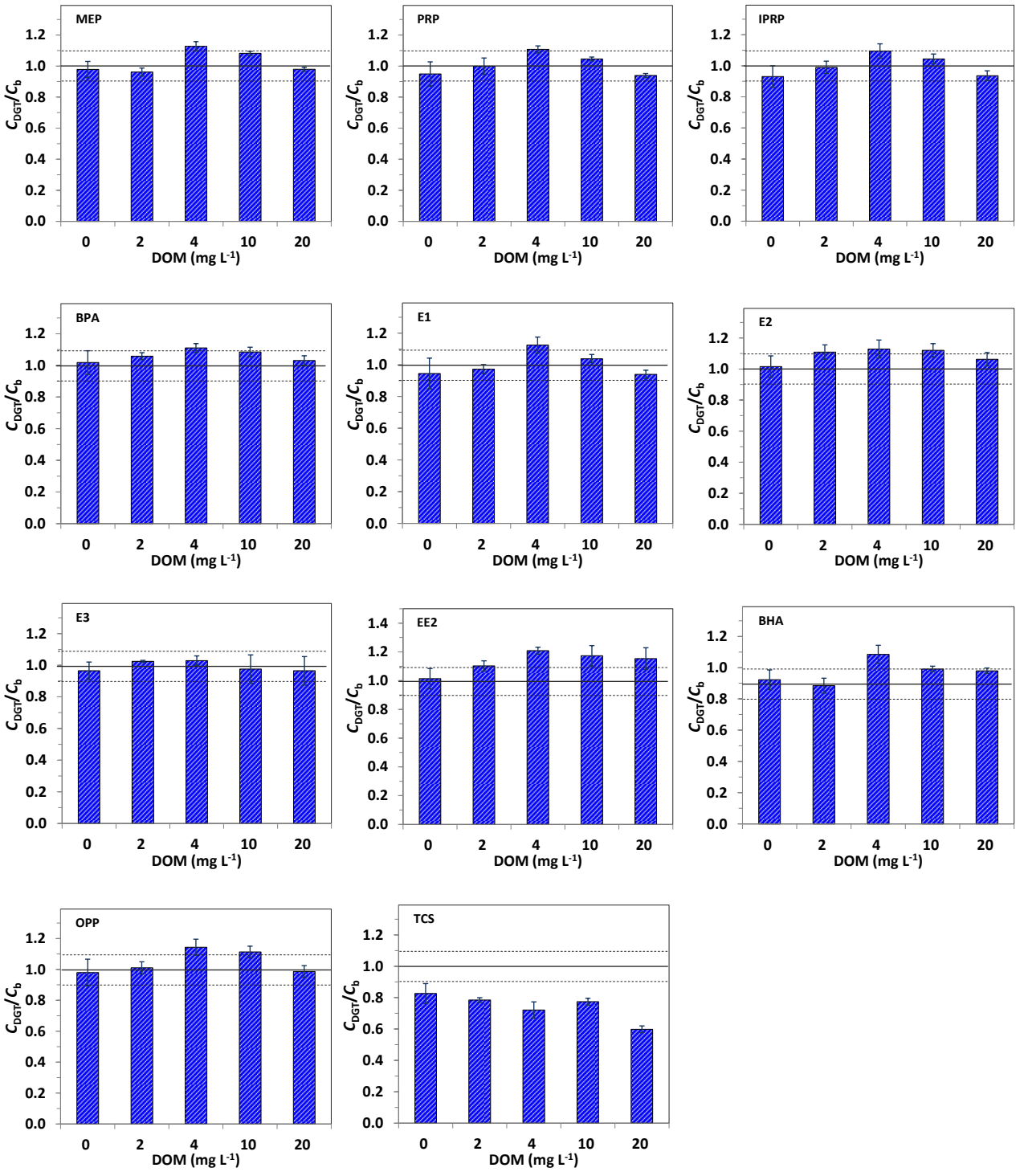

Figure S8: Effect of DOM on HLB-DGT measurement (pH = 6.9 ± 0.2, IS = 0.01 M, T = 20 ± 2 ℃; n = 3). C_{DGT} are the test chemical concentrations measured by DGT and C_b, are their concentrations in the bulk solutions. The solid horizontal lines represent the value of 1 and the dotted horizontal lines represent the values at 0.9 and 1.1. Error bars: 1SD.

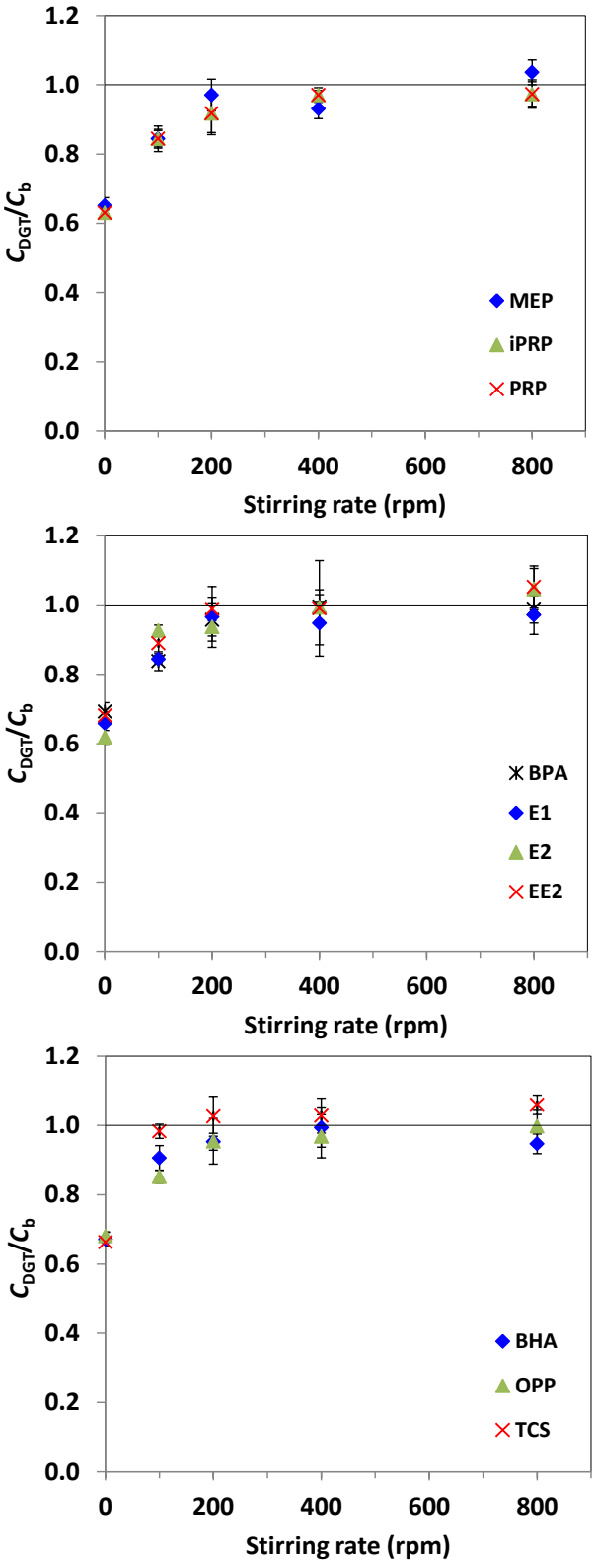

Figure S9: Effect of stirring rate on HLB-DGT measurement (IS = 0.01 M, pH = 6.5 ± 0.1 T = 23 ± 2 ℃; n=3). C_{DGT} are the test chemical concentrations measured by DGT and C_b are their concentrations in the bulk solutions. The solid horizontal lines represent the value of 1. Error bars: 1SD.

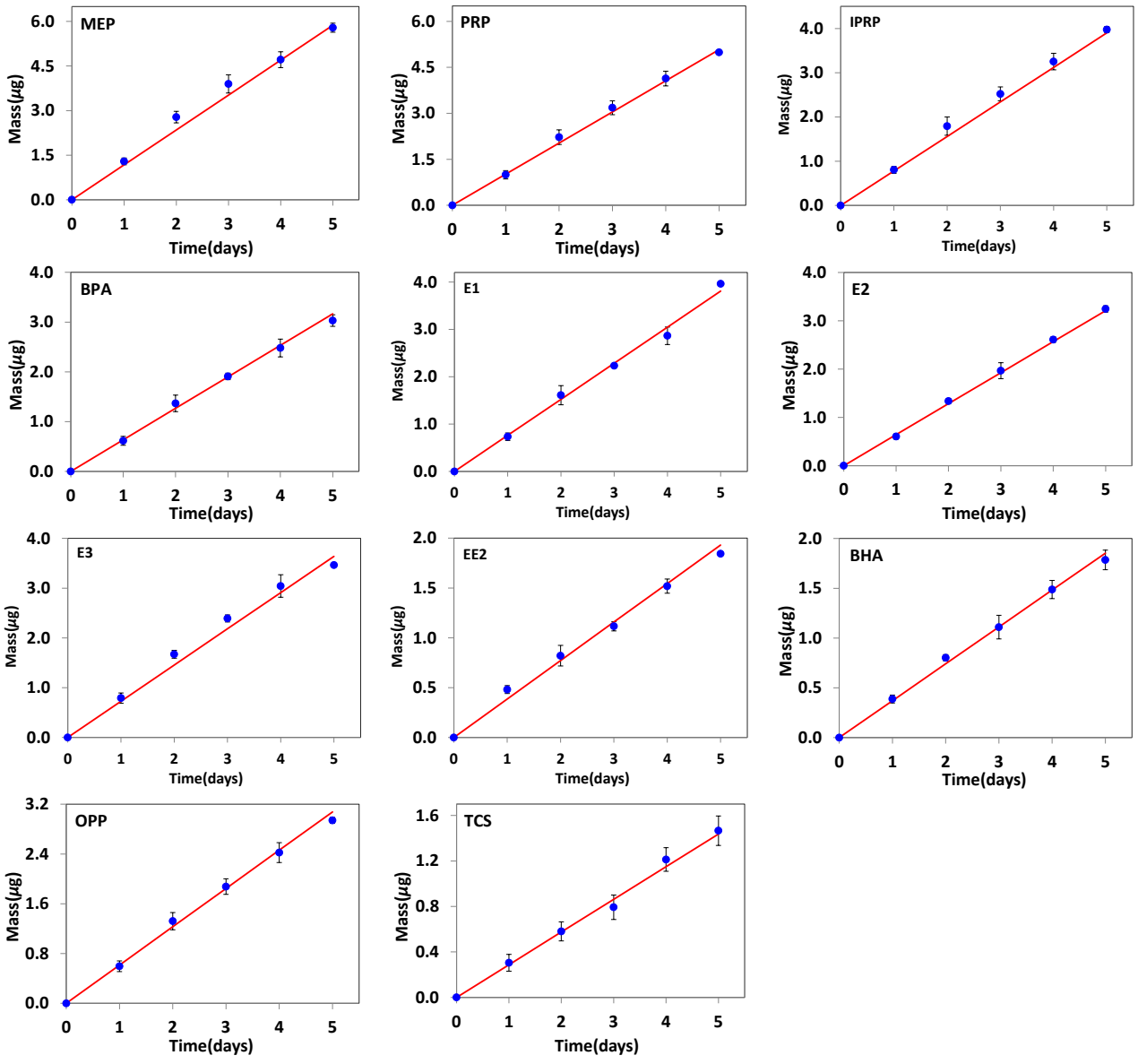

Figure S10: Measured masses (M, μg) of test chemicals in HLB-DGT deployed in well stirred solutions for different times (IS = 0.01 M, pH = 6.8 ± 0.2, T= 24 ± 2 ℃; n=3). The solid lines are theoretical lines predicted by equation (1). Error bars: 1 SD.

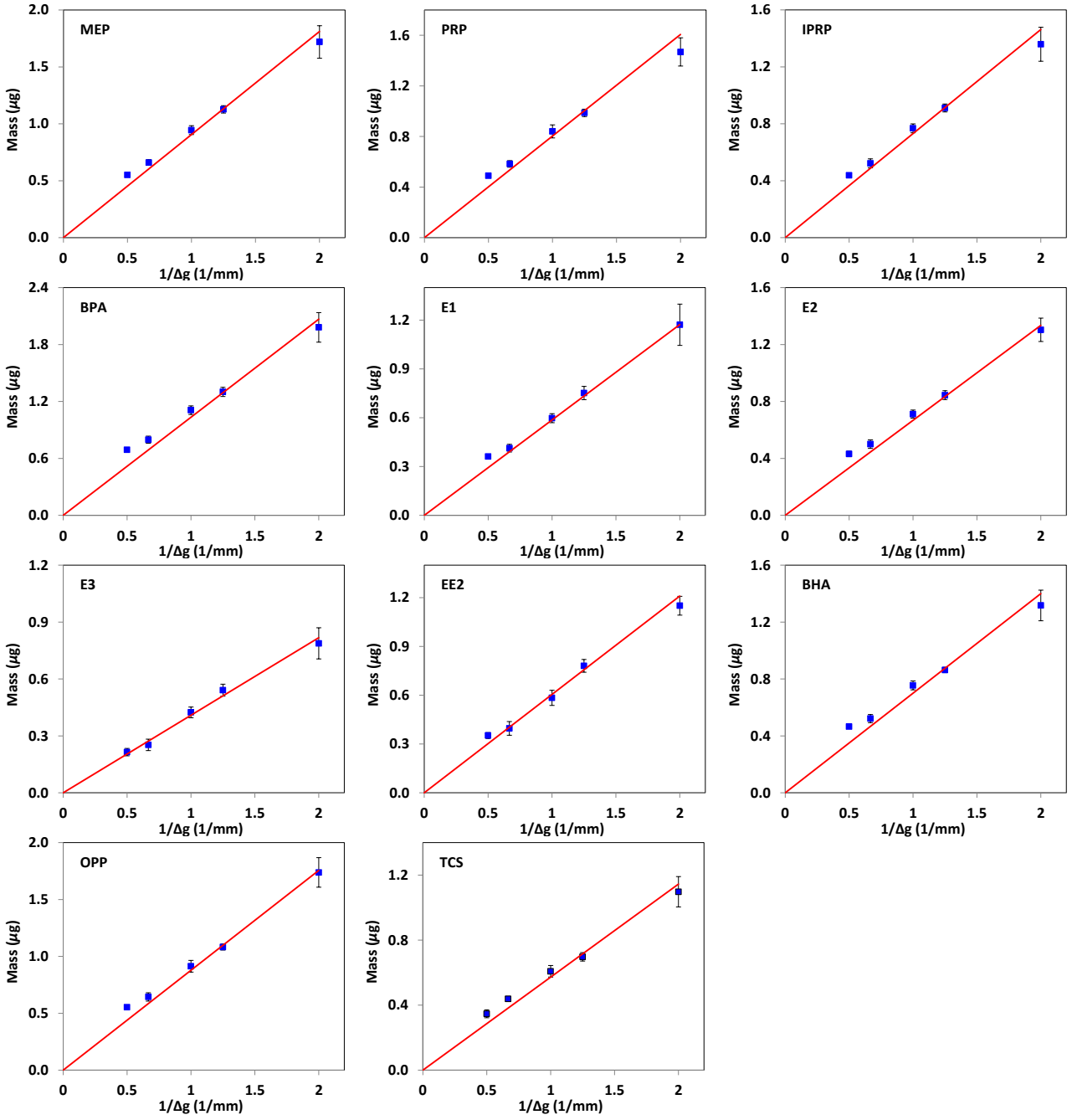

Figure S11: Measured masses (M, μg) of test chemicals accumulated in HLB DGT deployed in well stirred solutions with various diffusion layer thicknesses (IS = 0.01 M, pH = 6.8 ±0.2, T = 24 ±2 ℃; n=3). The solid lines are theoretical lines predicted by equation (1). Error bars: 1 SD.

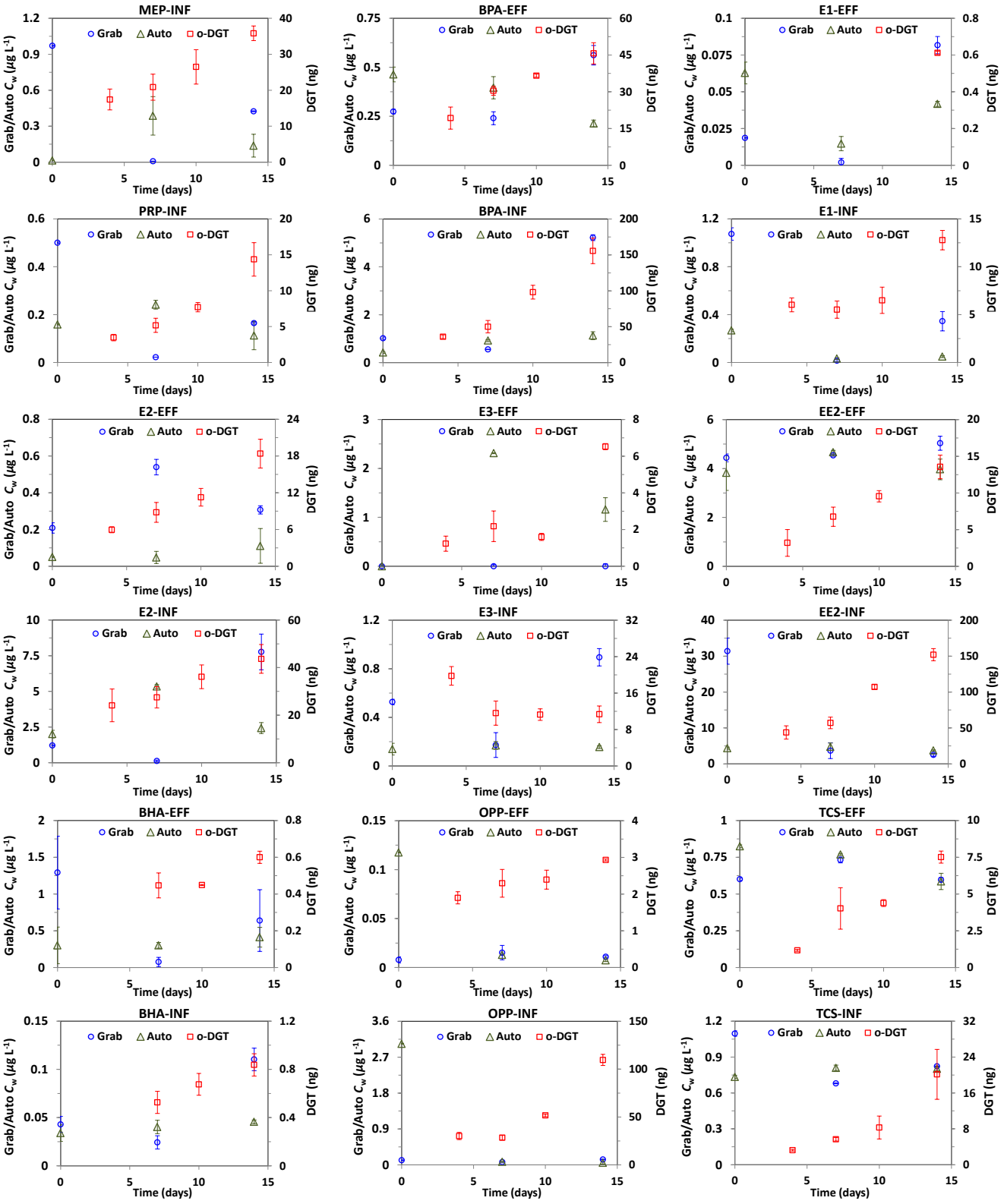

Figure S12: Typical test chemical uptake in DGT (right axis, n = 3) and water concentrations (C_w, left axis, Auto, auto sampling, n = 2; Grab, grab sampling, n = 2) of effluent and influent of a UK WWTP for 14 days. Error bar: 1SD.

277 References

278

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290
291

Paper II

Comparative Evaluation of DGT Samplers with Different Binding Resins for *in situ* Measurement of Trace Organic Chemicals in Waters

Comparative evaluation of DGT samplers with different binding resins for *in situ* measurement of trace organic chemicals in waters

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ABSTRACT

The selection of suitable resin as the binding agent is crucial for developing new DGT passive samplers. Three polymer-based resins which are potentially used in DGT techniques for organics, including hydrophilic-lipophilic-balanced (HLB), XAD18 and Strata-XL-A (SXLA) resins, were comparatively evaluated based on their uptake/sorption behaviours and the performance of the measurement for 11 test chemicals (preservatives, oestrogens, antioxidants and disinfectants) under different environmental conditions (pH, ionic strengths and dissolved organic matter) in the laboratory. The uptake experiment showed that XAD18 has the largest capacity for most of the test chemicals and the apolar interactions (van der Waals and π-π interactions) are the most important between the resins and the test chemicals. The performance of three types of DGT devices was reasonably independent of pH (3.5-8), ionic strengths (0.001 -0.1 M) and dissolved organic matter (0- 20 mg L^{-1}), but HLB and XAD18-DGT devices were more stable under different environmental conditions than SXLA-DGT. HLB-DGT was found to accumulate test chemicals consistent with theoretical predictions, while XAD18 and SXLA-DGT accumulated less amounts, indicating HLB-DGT could be directly and accurately applied to field measurement. Field application of three types of DGT devices was conducted in a wastewater treatment plant; the results confirmed the potential use of HLB-DGT sampler for *in situ* measurement of these test chemicals.

1. INTRODUCTION

The passive sampling technique of diffusive gradients in the thin-films (DGT), developed by Zhang and Davison in 1994,[1] has been demonstrated to be able to provide quantitative *in situ* measurements of the trace components in aqueous systems.[2] This sampling approach could provide accurate data for time-weighted average (TWA) concentration during the exposure in the aquatic environment. It has proved to be useful because of its simplicity and wide applicability over the last two decades.[3, 4] The DGT sampler could be directly applied in the field without *in-situ* calibrations, as the transport of the analyte is solely controlled by its molecular diffusion and the thickness of the diffusion layer,[1, 2] therefore this approach is insensitive to hydrodynamic conditions.[2, 3]

Theoretically, DGT can be applicable to any inorganic or organic diffusing species although almost all the results are focused on the inorganic measurement[3, 4] and few studies on organic measurements have been reported. Recently, several attempts have been made on the DGT measurements of organic substances. For example, Chen *et al.*[5, 6] successfully extended the application of DGT using XAD18 as the binding resin to measure 37 antibiotics in waters. Dong *et al.*[7, 8] subsequently used this sampler with molecularly imprinted polymers (MIP) as the binding agents to sample phenol and 4-chlorophenol (4-CP) in water. Zheng *et al.*[9] have also successfully applied DGT to 3 bisphenols (BPs) using activated charcoal as the binding layer. Fauvelle *et al.*[10] applied titanium dioxide (TiO_2) as binding phase for DGT to detect glyphosate (PMG) and aminomethyl phosphonic acid (AMPA) in the aquatic environment. More recently, we have developed a new DGT sampler with hydrophilic-lipophilic-balanced (HLB) resin as binding agent for detecting 11 trace organic chemicals (TOrCs) used in household products and pharmaceuticals

(including preservative, oestrogen, antioxidant and disinfectant) in wastewater.[11] **Table 1** summarises the recent DGT studies on organic compounds. It should be noticed that it is essential to select suitable materials/ resins when developing the DGT sampler for organic compounds or other passive samplers. These materials should possess large adsorption capacity and fast adsorption rate of target compounds and can perform stable in a wide range of pH and ion strength conditions.

Table 1: Recent DGT research for organic compounds in waters.

Target compounds	Resin	Diffusive layer	Filter	Capacity (μg per gel)	Applicable pH	Applicable IS, M	Ref
TOrCs	HLB	Agarose	polycarbonate	in this study	3.5-9.5	0.001-0.1	11
Antibiotics	XAD18	Agarose	Polyethenesulfone	360 for SMX	6.2-9	0.001-0.1	5, 6
Phenol, 4-CP	MIP	Nylon membrane	-	11.0 (phenol) and 31.5 (4-CP) mg/g	3-7	0.0001-0.1	7, 8
Bisphenols	Activated charcoal	Agarose	hydrophilic PTFE	140 (BPB), 190 (BPF) and 192 (BPA)	4.98-7.73	0.001-0.5	9
PMG, AMPA	TiO_2	Polyarylamide	Polyethenesulfone	2.57 (PMG) and 2.34 (AMPA)	5-8.5	UPW	10

The adsorption of organic compounds from the water phase onto the resins is a crucial process[12] which controls the performance of the passive water samplers (including DGT) for these compounds. It is important to investigate the driving forces of the adsorption processes and to have an insight to the mechanism, as this information is key for the selection of sorbent and predict suitability of sorbents for passive sampling.[13] We have previously developed a new DGT sampler for measuring the selected trace organic chemicals used in household products and of pharmaceuticals in the wastewater, but the sorption mechanism governing the sampler performance is poorly described and understood.

Therefore, the objective of this study is to 1) compare the performance of three DGT devices with different resins in laboratory condition for 11 test chemicals, 2) to investigate the sorption properties of

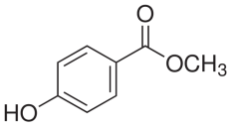
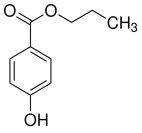
69 the resins and 3) to test and compare the in situ performance of different DGT devices in field conditions.

70 # 2. METHODS AND MATERIALS

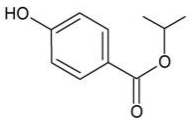
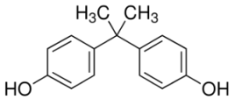
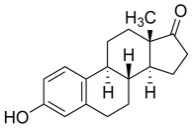
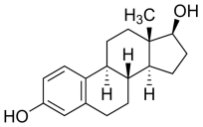
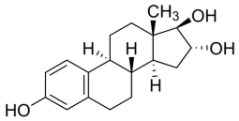
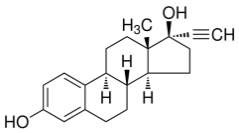
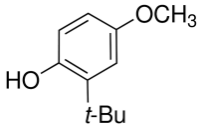
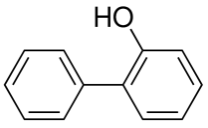
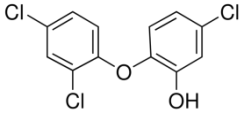
71 ## 2.1 Chemicals and Reagents

72 Eleven typical chemicals used in household products and of pharmaceuticals (preservative, oestrogen,
73 antioxidant and disinfectant) were selected as test chemicals in this study, which included methylparaben
74 (MEP), propylparaben (PRP), isopropylparaben (IPRP), bisphenol-A (BPA), estrone (E1), *β*-estradiol (E2),
75 estriol (E3), 17*α*-ethinylestradiol (EE2), butylated hydroxyanisole (BHA), ortho-phenylphenol (OPP) and
76 triclosan (TCS). Information of these test chemicals was given in **Table 2** (more detailed information is
77 listed in **Table S1**). Stock solutions for individual test chemicals standard (1000 mg L^{-1}) were prepared in
78 methanol and stored in sealed amber bottles in dark at -20 ℃ for later use. Working standard solutions (10
79 mg L^{-1}) were prepared weekly by diluting the stock solutions with methanol and stored at 4 ℃ before use.

80 **Table 2**: Information of test chemicals selected in this study and properties relevant to sorption[1].

Chemical	Structure	S_w / mgL^{-1} ($mmol\ L^{-1}$)[a]	*p*Ka[a]	$LogK_{OW}$[a]	SA, PSA, ASA / Å[2b]	ASA : PSA[b]	PA / Å[2b]	Aromatic bonds[b]
Methylparaben (MEP)		2500 (16.43)	8.31	2	349 47 303	6.5	23-53	6
Propylparaben (PRP)		500 (2.77)	8.23	2.98	414 47 368	7.9	30-60	6

[1] This table is continued onto the next page.

Chemical	Structure	S_w / mgL^{-1} ($mmol\ L^{-1}$)[a]	*p*Ka[a]	$LogK_{OW}$[a]	SA, PSA, ASA / Å^{2b}	ASA : PSA[b]	PA / Å^{2b}	Aromatic bonds[b]
Isopropylparaben (IPRP)		689.7 (3.83)	8.4	2.91	408 47 361	7.8	29-60	6
Bisphenol-A (BPA)		120 (0.53)	9.94/ 11.97	3.64	416 40 375	9.3	42-66	12
Estrone (E1)		30 (0.11)	10.33	3.43	396 37 359	9.6	42-83	6
β-estradiol (E2)		3.9 (0.014)	10.33	3.94	393 40 352	8.7	34-85	6
Estriol (E3)		440.8 (1.53)	10.33/ 13.62	2.81	398 61 337	5.6	38-88	6
17*α*-Ethinylestradiol (EE2)		11.3 (0.038)	10.33	4.12	408 40 368	9.1	40-90	6
Butylated hydroxyanisole (BHA)		212.8 (1.18)	10.55	3.5	394 29 365	12.4	36-59	6
Ortho-phenylphenol (OPP)		700 (4.11)	9.65	3.28	346 20 326	16.1	29-57	12
Triclosan (TCS)		10 (0.035)	7.68	4.66	413 29 384	13.0	40-71	12

a: the properties of solubility in water (S_w) at 25 ℃, acid dissociation constant (*p*Ka), octanol-water partition coefficient (Kow) were acquired from EPI Suite 4.1;

b: the properties of surface area (SA), apolar surface areas (ASA), polar surface area (PSA), projection area (PA) and aromatic bonds were calculated from MarvinSketch from ChemAxon.

Regents are at least analytical grade with ≥ 99% purity, organic solvents are HPLC grade. Sodium chloride (NaCl), sodium acetate (NaAc), sodium azide (NaN_3) and sodium bicarbonate ($NaHCO_3$) were also purchased from Sigma-Aldrich (UK). Hydrochloric acid (HCl, 35.5-37.5 %), sodium hydroxide (NaOH), ammonium acetate (NH_4Ac), methanol (MeOH) and acetonitrile (ACN) were obtained from Fisher Scientific (UK). Water used in the experiments was supplied from a Milli-Q water purification system (> 18.2 MΩ cm^{-1}, Millipore, UK). Gel solution for making DGT binding gels was prepared and provided by DGT Research Ltd (Lancaster, UK), ammonium persulfate (APS) and N,N,N′,N′-Tetramethylethylenediamine (TEMED) were purchased from Sigma-Aldrich (UK) and agarose were obtained from Bio-Rad Laboratories (UK). Descriptions on experimental details including the plastic-ware and glassware cleaning, pH and temperature measurement, the adjustment of pH, ionic strength (IS) and dissolved organic matter (DOM) concentration in the water solution, the sampling frequency, blank and control experiments setting, result data expression and statistical analysis and other setting were provided in the supporting information (**SI**).

2.2 Resins for DGT Binding Gels

Three types of resins were used in this study: HLB resins were extracted from Oasis-HLB solid-phase extraction (SPE) cartridges purchased from Waters Corporation (UK), XAD18 resins were purchased from Dow Chemical Company and Strata-XL-A (SXLA, a strong anion-exchange functionalised polymeric sorbent) resins were extracted from Strata-XL-A SPE tubes purchased from Phenomenex Inc(UK). All three types of resins are polymer-based. The properties, including specific surface area (SSA) and average particle diameter of three resins are listed in **Table S2**. The resins were thoroughly washed

105 with Milli-Q (MQ) water and then immersed in methanol followed by MQ water wash before use.

106 ## 2.3 DGT Preparation and Assembly

107 Diffusive gels (1.5 % agarose, 1.0 mm) and binding gels (0.4 mm, with HLB, XAD18 and SXLA resins
108 as the binding resins, respectively) used in DGT devices were prepared according to the well documented
109 procedures. [5, 11, 14] Polycarbonate membrane (PC filter, 10 μm of thickness, 0.2 μm of pore size, track-etch
110 membrane, Nuclepore, Whatman) was selected as the pre-filter as it did not adsorb the target chemicals
111 according to our previous study.[11] Binding gel sheets were washed in 1 L MQ water and hydrated in
112 another 1 L MQ water for about 24 h. The water was changed for 3-4 times. The sheets were then cut into
113 2.5 cm diameter disks and stored in 0.01 M NaCl solution at 4 ℃ before use.

114 ## 2.4 Chemical Analysis

115 The preparation of solution samples, the extraction of DGT samples for the laboratory experiments and
116 the analysis of these samples using a high performance liquid chromatography (HLPC) coupled with a
117 photodiode array detector (HPLC-DAD, Thermo Finnigan) were conducted following the procedures
118 from a previous literature.[11] The extraction of the field DGT samples[14] and their analysis using liquid
119 chromatography-tandem mass spectrometer (LC-MS/MS, Waters, UK)[15] were conducted according to
120 published procedures with minor optimisation.

121 ## 2.5 Theory Section

122 ### *2.5.1 Sorption theory*

123 The interactions between target compounds and resins in the water solution play important roles in

sorption, such as van der Waals, Coulomb, π-π interaction and hydrogen bonding (H-bonding). The van der Waals interaction, occurring between all molecules and functional groups, is normally weaker than H-bonding which happens between hydrogen donor and acceptor groups. The π-π interaction only happens among the aromatic rings, and the Coulomb forces are electrostatic interaction which affect between charged groups/ molecules.

Equilibrium sorption models, like Langmuir, Freundlich and Redlich-Peterson models,[16] were used to describe the equilibrium between aqueous concentrations (C_w, mmol L^{-1}) of the test chemicals in the solution and the concentrations (q_e, mmol kg^{-1}) on the sorbent/ resin, and they were also used to explain the possible mechanism of sorption processes in this study. Among these models, Langmuir model described in Equation (**1**), was preferred as the maximum sorption capacity (Q_{max}, mmol kg^{-1}) of test chemicals,[13] which means the gel uptake capacity in this study, could be estimated:

$$q_e = \frac{K_L \cdot Q_{max} \cdot C_w}{1 + K_L \cdot C_w} \quad (1)$$

where K_L (L $mmol^{-1}$) is a constant reflecting the equilibrium of the sorption process.

The kinetic sorption models, including two reaction-based models (pseudo-first-order and pseudo-second-order models)[17] and a diffusion-based model (Weber-Morris model)[18] were also employed to describe sorption kinetics of test chemicals.

2.5.2 DGT principle

A typical DGT device is composed of a backing cylinder and a front cap with a 2 cm diameter exposure window. A resin gel, a diffusive gel and a protective filter were placed successively and securely between

143 the top of the cylinder and the back of cap. The principle of DGT technique is based on the Fick's first
144 law of diffusion.[2, 3] The DGT measured concentration, C_{DGT}, is the TWA concentration of organics during
145 deployment. It could be simply expressed using Equation (**2**) when the thickness of diffusive boundary
146 layer DBL (δ) is much less than the thickness of the diffusive layer (Δg) under most conditions:[2]

147 $$C_{DGT} = \frac{M\Delta g}{D_e A t} \quad (2)$$

148 where M is the measured mass of test chemical accumulated in the binding gel layer, D_e is the diffusion
149 coefficient of test chemical in the diffusive gel, t is the exposure time and A is the exposure window area
150 of the cap.

151 ## 2.6 Experimental Section

152 The experiments were conducted not only to compare the performance among the three different types of
153 DGT devices with various resin gels, but also to help to understand the sorption behaviours of test
154 chemicals on these three resins under different conditions. These tests included four aspects: 1) binding
155 gel uptake capacity and uptake kinetics, 2) extraction recoveries for three resin gels, 3) effects of pH,
156 ionic strength and dissolved organic matter on performance and 4) time dependence for uptake. The
157 procedures of these tests were detailed described in our previous study[11] and introduced briefly below:

158 **Binding gel uptake capacity and uptake kinetics**: The DGT devices (a 0.4 mm HLB, XAD18 or SXLA
159 resin gel in the front of a 1.0 mm diffusive gel) were exposed to 50 mL solutions of various
160 concentrations of the test chemicals to investigate the uptake capacity. All the solutions (pH = 6 or 8)
161 were shaken for 24 h. The adsorbed amounts of test chemicals by resin gels were calculated according to

the differences of the test chemical concentrations before and after the experiment. Uptake kinetics were investigated by placing and shaking the different binding gels in 20 mL of 200 μg L^{-1} test chemical solutions for different times. Sample of 0.1 mL solution was collected each time during a period of 24 h.

Recoveries of extraction for three resin gels: HLB, XAD18 and SXLA resin gels were added into 10 mL solution with three different concentrations of test chemicals (100, 250 and 500 μg L^{-1}), respectively and shaken for 24 h on the shaker. The binding gels were then taken out and extracted in the ultrasonic bath with 5 mL ACN for 30min according to a previous study.[11] The recoveries were then calculated to confirm whether the extraction method could achieve good recoveries for all these three resin gels with various adsorption amounts of test chemicals.

Effects of pH, IS and DOM: DGT devices were deployed in 2 L of ca. 100 μg L^{-1} test chemical solutions with different pH (3.5-9.5), IS (0.001 M – 0.5 M) and DOM contents (humic acid, 0-20 mg L^{-1}) for 20 h. The ratio of C_{DGT} to the directly-measured concentration (C_b) of test chemicals in the solution was used to evaluate the performance of DGT under different conditions. The ratio of C_{DGT}/C_b between 0.9-1.1 indicates good performance of DGT.

Time dependence: DGT devices (1.0 mm agarose diffusive gel and 0.4 mm resin gel) were deployed in a test chemical solution at 24 ± 2 ℃ of ca. 50 μg L^{-1} for different time (up to 5 days). The resin gels were taken out and extracted, and the amounts of test chemicals accumulated in binding gels were measured.

2.7 Field Evaluation in WWTP

HLB-DGT devices have been evaluated in a previous study,[14] which confirmed the HLB-DGT could be

effective for routine monitoring of the test chemicals and provide reliable TWA concentrations of the test chemicals in the wastewater. To evaluate the applicability of DGT in the field, XAD18-DGT and SXLA-DGT as well as HLB-DGT devices were deployed for up to 2 weeks at both influent and effluent (ca. 30 cm below the water surface) in a British WWTP. The average water temperature was 9.6 ℃ during the deployment. DGT samplers were retrieved at Day 4, 7, 10 and 14 from each site, rinsed with MQ water and then sealed in a clean plastic bag for transport. Once arrival at the laboratory, the DGT binding gels were taken out and extracted. Field blank samples of three types of DGT were also prepared and taken to the WWTP without deployment. DGT sample pre-treatment and LC- MS/MS analysis were conducted following the published procedures.[14, 15]

3. RESULTS AND DISCUSSION

3.1 Binding Gel Capacity and Uptake Kinetics

3.1.1 Sorption behaviour

The experiment results (**Figure S1**) showed that the uptake by XAD18 and SXLA resin gels for all 11 test chemicals could increase linearly in the range of 1-2 mg L^{-1} concentrations of solution at both pH 6 and 8, which is similar with the phenomenon observed in our previous study,[11] and there were not significant differences of uptake in these ranges of concentrations for all three resins. The differences of uptake appeared among the resin gels as well as between two pH systems after the linear phase and the uptake rate became slow although the resin gels could still continue to uptake with increasing solution concentrations. TCS could be linearly taken up by all three types of resin gels in both solutions for the

whole range of the concentrations during the entire experiment, indicating that it did not reach the capacities of the resin in this experiment.

Based on the uptake experiments, the sorption models were applied to explain the differences observed among three resin gels. The parameters for each model are listed in **Table S3**. It was found that better fitting of Redlich-Peterson (correlation coefficients, R^2 closer to 1,) was observed comparing with other two models for the majority of test chemicals, indicating that the heterogeneous pores and surfaces of the resins could play an important role for sorption process for all these three resins. The Langmuir model also fits well with the experimental data (with $R^2 > 0.9$ for most data), thus the maximum sorption capacity (Q_{max}) of three different resins for individual chemical (except for TCS) was estimated according to the Langmuir model and listed in **Table S3**. It could be noticed that the XAD18 rein has the largest Q_{max} for all test chemicals (except for BPA and OPP at pH 6) in both pH systems and SXLA has the smallest capacity at pH 6 for majority of test chemicals (except for E1 and E2). This is because XAD18 resin has the largest SSA while SLXA has smallest one (larger SSA could provide more sorption sites), which also confirmed that the importance of pores and surfaces of resins on sorption. Furthermore, the lower apolar fraction of SXLA resin (it contains some polar fractions for the ion-exchange), which reduced the sorption sites, could be another reason for the smaller Q_{max} in pH 6 solution.[13] Much larger Q_{max} was observed when HLB and XAD18 resins adsorbed test chemicals in pH 6 than in pH 8 (except for E1 and E2), indicating that the HLB and XAD18 could better perform under acid conditions.[19] The better performance of HLB resins under pH 6 is also confirmed from the manual that the resins were recommended to operate under the acid condition when used for SPE. While no significant change of

220 Q_{max} was observed for SXLA when pH increased from 6 to 8, indicated the decline of van der Waals
221 interaction and/or increasing of Coulomb force for SXLA retention in alkaline conditions.

222 *3.1.2 Impact of functional groups*

223 The performance of each resin gel on uptake/sorption of different test chemical could be used to elucidate
224 the significance of functional groups of test chemical and the resin and then figure out the dominant
225 interaction in controlling the sorption behaviour. The order of Q_{max} of three resins for the test chemicals
226 (**Table S3**) were generally consistent when pH increased from 6 to 8, indicating that the pH has no great
227 effect on the functional groups interaction between resins and the test chemicals. While the differences of
228 Q_{max} between two pH values for the same resin could indicate the impact of functional groups on
229 uptake/sorption behaviour. For example, the larger Q_{max} under pH 6 than in pH 8 for HLB resins indicated
230 that the apolar interactions are dominant to control the uptake/sorption of these chemicals by HLB resins,
231 since these chemicals are ionisable and more neutral fraction exists at pH 6 than at pH 8. This also
232 indicated that the Coulomb force is not so important for HLB uptake/sorption, as anionic proportion
233 increased with pH, but Q_{max} declined with pH.

234 OPP and E3, which have largest and smaller number of aromatic bonds and ratio of ASA/PSA,
235 respectively, were observed largest and smallest Q_{max} among all test chemicals (except TCS) for all three
236 resin gels in two pH systems. This result indicated that apolar interactions (van der Waals and π-π
237 interactions) are the most important interactions between test chemicals and resins. The *p*Ka of OPP and
238 E3 was 9.65 and 10.33 (**Table 2**), this means they are both neutral at both pH systems and there is no
239 Coulomb force between these two chemicals and resins. The H-bonding should be also less important as

E3 owns largest number of H-donor/acceptor while OPP owns smallest one (**Table S1**). BPA has the same aromatic bonds as OPP, but smaller ratio of ASA/PSA, which led to the smaller Q_{max}. BPA has more aromatic bonds but smaller ratio of ASA/PSA than BHA, showing a larger Q_{max} than BHA for HLB, indicating the π-π interaction is dominant for HLB.

For oestrogen chemicals, the Q_{max} was listed as EE2 > E2 > E1 > E3 for all three resin gels in both two pH system. They have the same aromatic bonds, but E1 has the largest SA and projection area allowing most interaction sites with polymer resins. For parabens, the Q_{max} was listed as PRP > IPRP > MEP. PRP has largest SA and ratio of ASA/PSA will enhance the van der Waals interaction between paraben and resins.

According to the structures of the resins (**Table S2**), the apolar interactions (van der Waals and π-π interactions) should be dominant interactions between the resins of XAD18 and HLB, and the compounds, which are also confirmed by the uptake/sorption results. These two resins may be able to suitable for neutral compounds (in this study) and compounds which owns the more aromatic bonds. While the Coulomb force may act important role for SXLA resin since it is a strong anion mixed polymer, which is more potentially interact with the ionised compounds.

3.1.3 Binding gel capacity estimation

The uptake capacity per resin gel disc can be calculated according to the Q_{max} estimated by the Langmuir model and resin amounts in each resin gel disc. The smaller results for individual chemicals in two different pH systems were used to estimate this uptake capacity for each resin gel, which was shown in **Table S4** (the maximum results in the experiments used for TCS, but not the capacity actually). The

capacity of HLB, XAD18 and SXLA-DGT devices ranged from 17.0 (MEP) to 196 μg (BHA), 28.7 (MEP) to 207 μg (BHA) and 23.4 (MEP) to 219 μg (BHA), respectively. Subsequently, the projected deployment period of the DGT devices and the projected concentrations could be roughly calculated based on the capacities. Normally, the environmental concentrations for these compounds are at the level of ng L^{-1}, even for the extreme conditions, assuming the concentration of 10 μg L^{-1}, the projected maximum deployment times for three HLB, XAD18 and SXLA-DGT devices would be at least 3, 5 and 4 months, respectively. However, considering the coexistence of other adsorbed compounds and the possibility of biofouling in the aquatic environment, a practical shorter deployment period (eg. 2 weeks~1 month) would be more likely. Thus, the projected maximum measurable concentrations in the aquatic environment can be as high as 31, 52 and 42 μg L^{-1} when HLB, XAD18 and SXLA-DGT devices were used to measure all the test chemicals.

3.1.4 Uptake kinetics

The results of binding kinetics (**Figure 1**, full set in **Figure S2**) showed that the uptake of test chemicals by each resin gel increased rapidly with time for the first hour, followed by a relatively slow increase. The uptake onto XAD18 resin gel was slightly faster than that of the HLB resin gel and much faster than that of SXLA resin gel, except MEP. It indicated that XAD18 and HLB could be more suitable as binding phases for the test chemicals for the DGT development, while SXLA may not suitable as binding phase. This was also confirmed by further test on the time dependence. For estrogenic compounds (E1, E2, E3 and EE2), both XAD18 and HLB gels could adsorb test chemicals faster than SXLA gel, and there were no significantly differences (ANVOA, $p > 0.05$) on uptake between XAD18 and HLB gels. A complete

uptake of all the compounds was nearly obtained in 12 h for XAD18 (except MEP) and in 24 h for HLB, while only about 90 % adsorption efficiencies of most compounds was achieved for SXLA resin.

The fitting of kinetic models is shown in **Table S5**. It is evident that that the uptake kinetics of all test chemicals by three resin gels are better fitted with the pseudo-second-order model by better R^2, Weber-Morris model also has better fitting comparing with pseudo-first-order model. When the pseudo-second-order model is used to describe the sorption kinetics, XAD18 and SXLA resins were observed with best and worst R^2 and highest and lowest rate constants (except MEP), respectively. These results confirm that the most sorption sites of XAD18 resin could provide fastest sorption of the test chemicals, but inverse of SXLA resin. The good R^2 were also observed of SXLA resin for Weber-Morris model, which indicated that diffusion could also be important sorption kinetics mechanisms for SXLA resin, but less important for XAD18 and HLB resins.

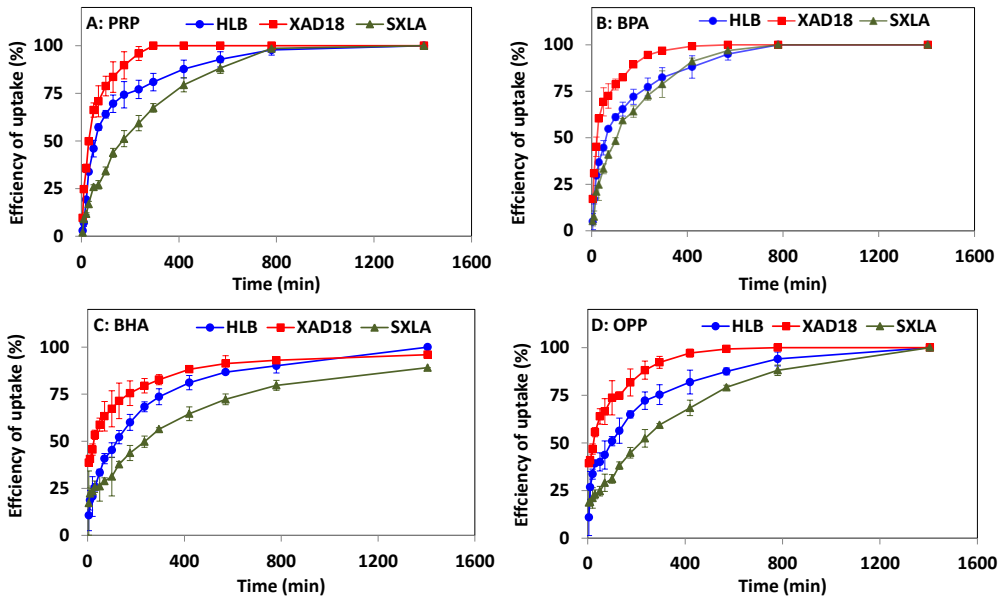


Figure 1: Dynamic binding of selected test chemicals by HLB, XAD18 and SXLA resin gels in 20 mL solutions of 200 μg L^{-1} test chemicals (n=3). Error bars were calculated from the standard deviation (SD) of three replicates.

3.2 Extraction Recoveries

The extraction recoveries of the test chemicals were investigated at three concentrations for HLB, XAD18 and SXLA resin gels to test the recovery stability for different concentrations and gels according to the previously optimised procedure.[15] The recovery results of the test chemicals for HLB, XAD18 and SXLA gels are shown in **Table S6**, ranging from 64.6 ± 5.0 % to 123 ± 11.1 %, 69.0 ± 7.0 % to 122 ± 8.8 % and 64.2 ± 6.9 % to 118 ± 12.2 %, respectively. These results indicate that the ultrasonic extraction with ACN can achieve good and reproductive recoveries for these three types of gels. Similar and consistent recoveries (**Table S6**) were observed for individual chemical among three resin gels at three different concentrations (100, 250 and 500 μg L-1) of solutions, to simplify the calculation, the overall recoveries (calculation of HLB, XAD18 and SXLA resins together) were used for all three types of binding gels, and the averages of overall recoveries (**Table S6**) were ranged from 65.9 ± 6.6 % (BHA) to 121 ± 9.2 % (MEP).

3.3 Effects of pH, IS and DOM

3.3.1 Effect of pH

The pH effects on three types of DGT measurement for test chemicals are presented in **Figures 2** and **S3**, showing The values of C_{DGT}/C_b at the same pH were generally listed as XAD18 ≥ HLB > SXLA for the majority of test chemicals (except MEP). This phenomenon can result from the differences of test chemical uptake efficiency among three various binding gels. Values of C_{DGT}/C_b (**Table S7**) fell within 0.9-1.1 for HLB and XAD18-DGT from pH 3.5 to 9.5 in most circumstances, but less for SXLA-DGT.

313 The ratio of C_{DGT}/C_b for XAD18 and SXLA-DGT showed a slight decline with the increasing pH, which
314 is similar with HLB DGT.[11] Significant difference (ANOVA, $p < 0.05$) of C_{DGT}/C_b for HLB and XAD18
315 DGT was not observed when pH was changed for the majority of test chemicals, but observed for SXLA
316 DGT when pH increased to 9.5. D_e values measured at pH 3.5 and 9.5 showed no significant difference
317 (ANOVA, $p > 0.05$) with the D_e at pH 6.8. Thus, the reason of C_{DGT}/C_b decline for XAD18 and HLB
318 resins could be the stronger retention of the test chemicals in acid condition[19] and the lower proportion of
319 test chemicals bound anionically to the resin gels due to the electrostatic repulsion[20] at higher pH
320 conditions condition, which is confirmed from the binding capacity experiments and discussed in section
321 of *Sorption behaviour* (3.1.1). Similar phenomena were observed when HLB-POCIS was used for
322 sampling endocrine disturbing chemicals (EDCs, e.g. E1, E2, EE2 and BPA) [21] and MAX-POCIS (MAX,
323 similar to SXLA, a mixed-mode anion-exchange and reversed-phased sorbents) for phenols and
324 oestrogens,[22] and when XAD18 was used as binding resin for DGT to measure the antibiotics in water.[5]
325 SXLA resin was designed for SPE extraction of weak acids and the SXLA-DGT was expected to have
326 better performance at higher pH, while showed the larger decline than XAD18 and HLB, indicating that
327 the greater impact on SXLA-DGT performance resulted from the reduction of reserved-phase retention
328 than from the enhancement of ion-exchange retention at higher pH condition. Overall, HLB and
329 XAD18-DGT have similar and stable performance in wide range of pH (3.5-9.5), which is relatively
330 better than SXLA, indicating they have potential for direct measurement of the test chemicals in the field
331 conditions.

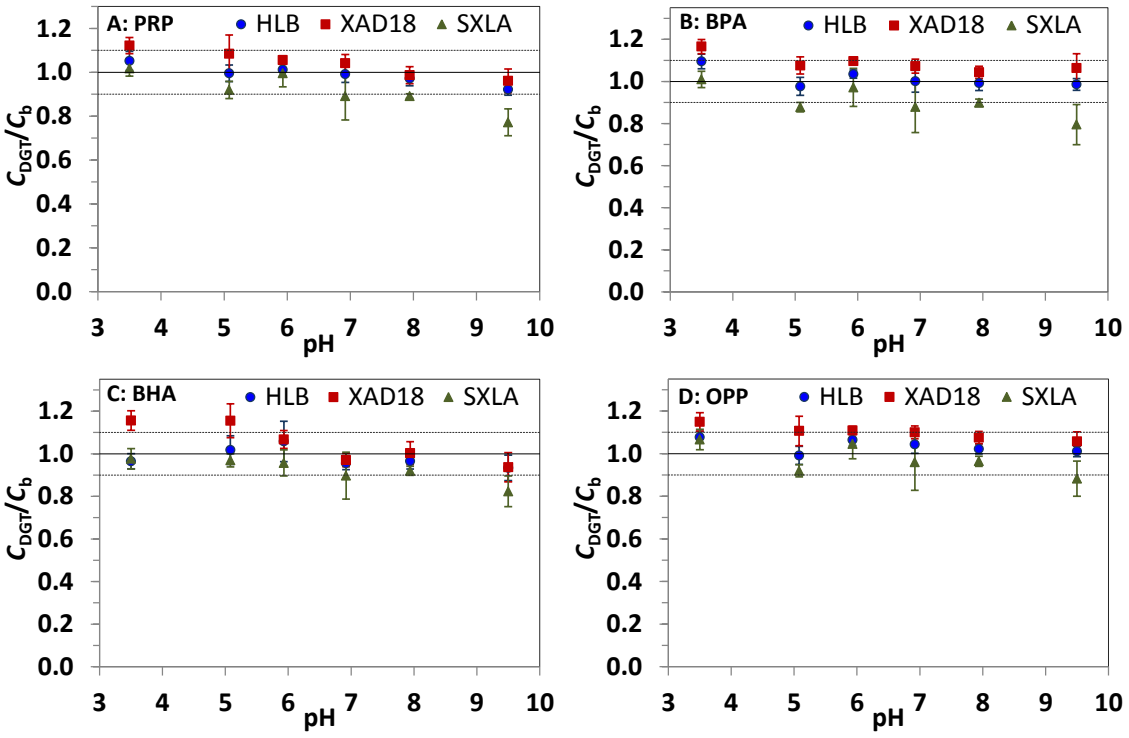


Figure 2: pH effect on measurement of DGT with HLB, XAD18 and SXLA binding gels (n = 3). Error bars: 1SD.

3.3.2 Effect of IS

The effect of IS on DGT performance for the test chemicals is shown in **Figures 3** and **S4**, and the values of C_{DGT}/C_b were listed as XAD18 ≥ HLB > SXLA for the majority of the test chemicals, which can also be explained by the differences in uptake efficiency of the test chemicals among three various binding gels. For all three types of DGT devices, the values of C_{DGT}/C_b (**Table S8**) fell within 0.9-1.1 when IS concentration was 0.001-0.1 M in most circumstances, and there were no significant differences (ANOVA, p>0.05) for the majority of the test chemicals within this range of concentrations. A significant reduction (>10 %) of C_{DGT}/C_b was observed when IS increased to 0.5 M, but the D_e measured at IS = 0.5 M solution was not significantly different with D_e at IS = 0.01 M. Therefore, the reason for this decline can be that the test chemicals were weakly binding to the resin gels due to the competition/coexistence with the high

concentration of Cl^- in the solution. The salting-out effect caused by presentation of NaCl, which will reduce the solubility and the dissolved fraction of the test chemicals in the solution, could be another reason for the decline. This phenomenon also was observed when XAD18-DGT used for antibiotics[5] and activated charcoal based DGT for BPs.[9] While it was contrast to Dong *et al.*'s research on 4-CP using MIP-DGT.[8] Thus, the results indicate that the sampling of test chemicals by three DGTs was independent of IS in the range of 0.001 to 0.1 M, and HLB and XAD18-DGT could be more stable within the experimental concentrations of IS when comparing with SXLA-DGT, but all of them can be best applied to the freshwater (IS ca. 0.01M) sampling. Further work is needed for using DGT to measure those chemicals in seawater (IS ca. 0.6M).

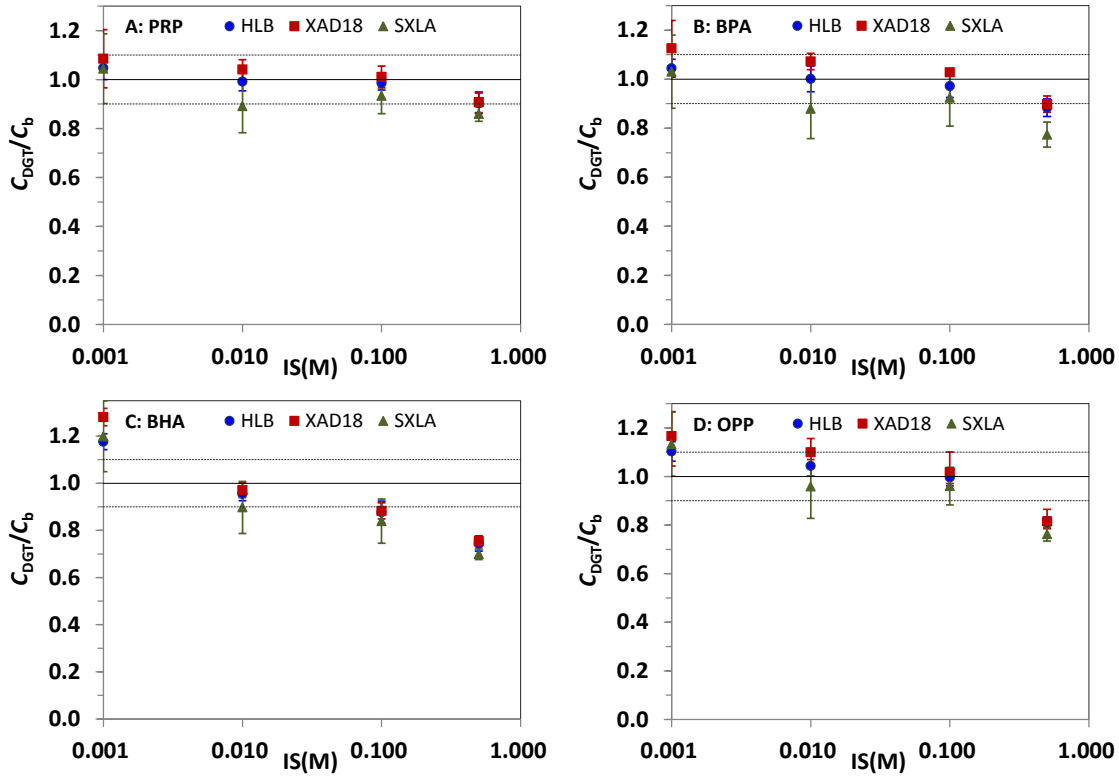
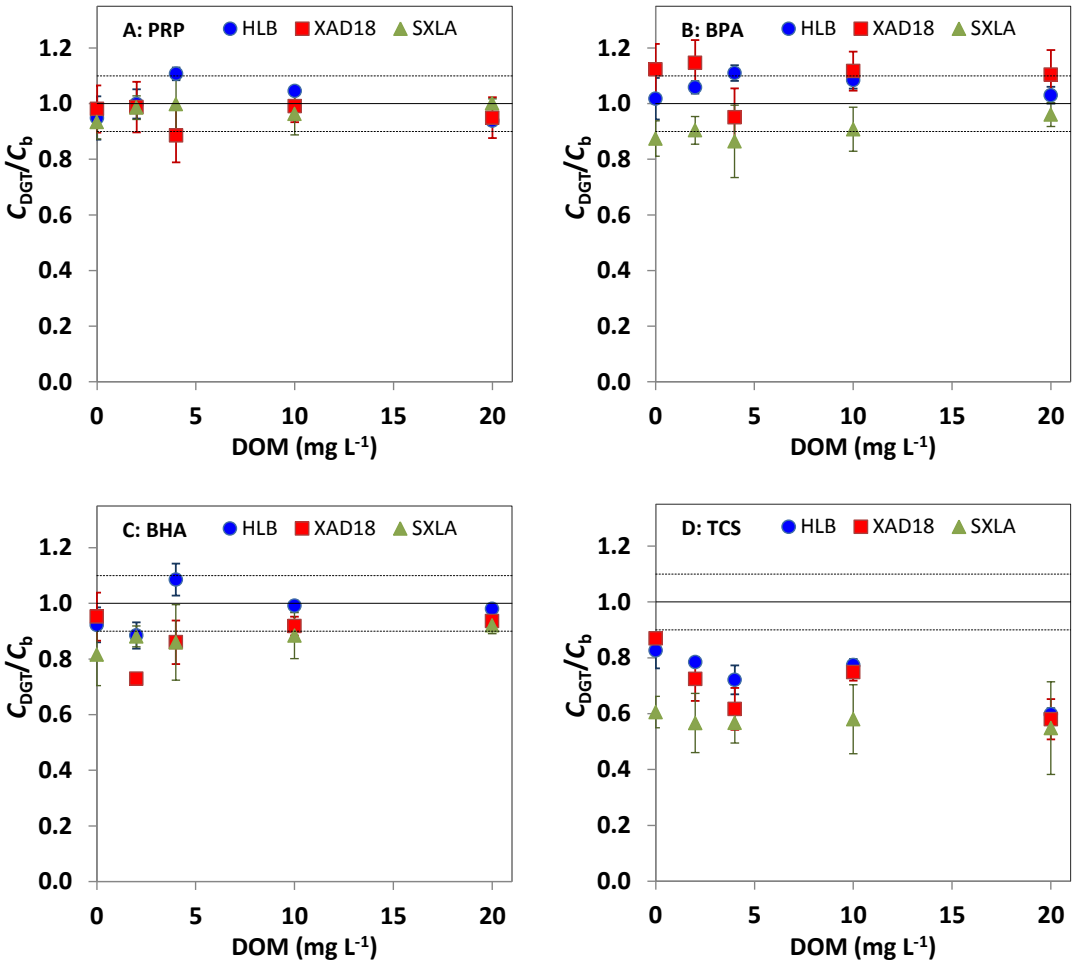


Figure 3: Effect of IS on DGT performance for HLB, XAD18 and SXLA binding gels (n = 3). Error bars: 1SD.

3.3.3 Effect of DOM

The performance of three DGT devices in the solution with different DOM concentrations (**Figures 4, S5 and Table S9**) showed that the values of C_{DGT}/C_b were generally listed as HLB > XAD18 > SXLA for the majority of test chemicals. No significant change (ANOVA, p>0.05) of C_{DGT}/C_b ratios was observed for individual DGT when DOM concentration was in the range of 0-20 mg L^{-1}, which was consistent with several previous studies on the POCIS uptake in the presence of DOM.[22, 23] For HLB-DGT, the values of C_{DGT}/C_b for the test chemicals increased when the small amount of DOM existing (0-4 mg L^{-1}) and then decreased when the DOM concentration increased (above 4 mg L^{-1}) except TCS. This result was consistent with Li *et al.*'s study[22] on increased uptake of pharmaceuticals by HLB-POCIS when DOM increased from 3.33 to 4.92 mg L^{-1} and also agreed with the Dong *et al.*'s research[8] showing the reduced ratios of C_{DGT}/C_b at high DOC contents (9.8- 36.5 mg L^{-1}). Opposite trend on uptake was found for XAD18-DGT, the value of C_{DGT}/C_b for most test chemicals declined when the small amount of DOM existing (0-4 mg L^{-1}), but increased with higher the DOM concentration (above 4 mg L^{-1}). The C_{DGT}/C_b ratio of SXLA-DGT changed differently with HLB and XAD18-DGT, showing a general increasing trend. All these indicated the different interactions between various resin gels and the test chemicals at the presence of DOM. In summary, HLB and XAD18-DGT devices were relatively more stable and performed better than SXLA-DGT, and they can be used in aquatic environment with wide range of DOM concentration for majority of test chemicals.



373

374 **Figure 4:** Effect of DOM on DGT measurement for HLB, XAD18 and SXLA binding gels (n = 3). Error bars: 1SD.

375 ## 3.4 Time Dependence

376 The 5-day experiment for time dependence was conducted to confirm the validity of DGT principle for
377 the test chemicals. The results in **Figures 5 and S6** showed the general order of accumulated mass by
378 three types of DGT devices was: HLB ≥ XAD18 > SXLA for all the test chemicals (except XAD18 for
379 MEP for and SXLA for BHA). The HLB-DGT simultaneously and continuously accumulated test
380 chemicals and the accumulated masses increased linearly (R^2 ranged from 0.9853 to 0.9995, $p < 0.001$)
381 with the deployment time, which agreed well with the theoretical prediction. XAD18 and SXLA-DGT

could also approximately accumulate the test chemicals linearly with the deployment time for most of the chemicals (except MEP and BHA, slow uptake of MEP by XAD18 and BHA by SXLA could be a possible reason), but below theoretical lines. Although there was no significantly difference (ANOVA, $p > 0.05$) on accumulation mass in 24 h among these three DGT devices, XAD18 and SXLA-DGT accumulated much less amounts of most test chemicals than HLB-DGT for longer deployment time (**Figure S6**). The measured-to-predicted ratios of XAD18-DGT and SXLA-DGT ranged from 0.21 ± 0.02 (MEP) to 0.96 ± 0.03 (EE2) and from 0.39 ± 0.05 (BHA) to 0.73 ± 0.05 (IPRP) at the end of the 5^{th} day, respectively. The possible reasons could be 1) the different uptake efficiencies of the binding resins (slowest uptake of SXLA) and this difference will significantly appear when the DGT were deployed for a long period of time, and 2) competitive binding of chemicals on HLB and XAD18 resin gels (it has been confirmed by the time dependence for individual chemical taking E3 and BHA as examples separately). According to the time-series results, it indicated that HLB-DGT can be used for measurement of all 11 test chemicals in aquatic system directly and accurately, while XAD18-DGT and SXLA-DGT may not suitable for monitoring unless correction or calibration factors are used.

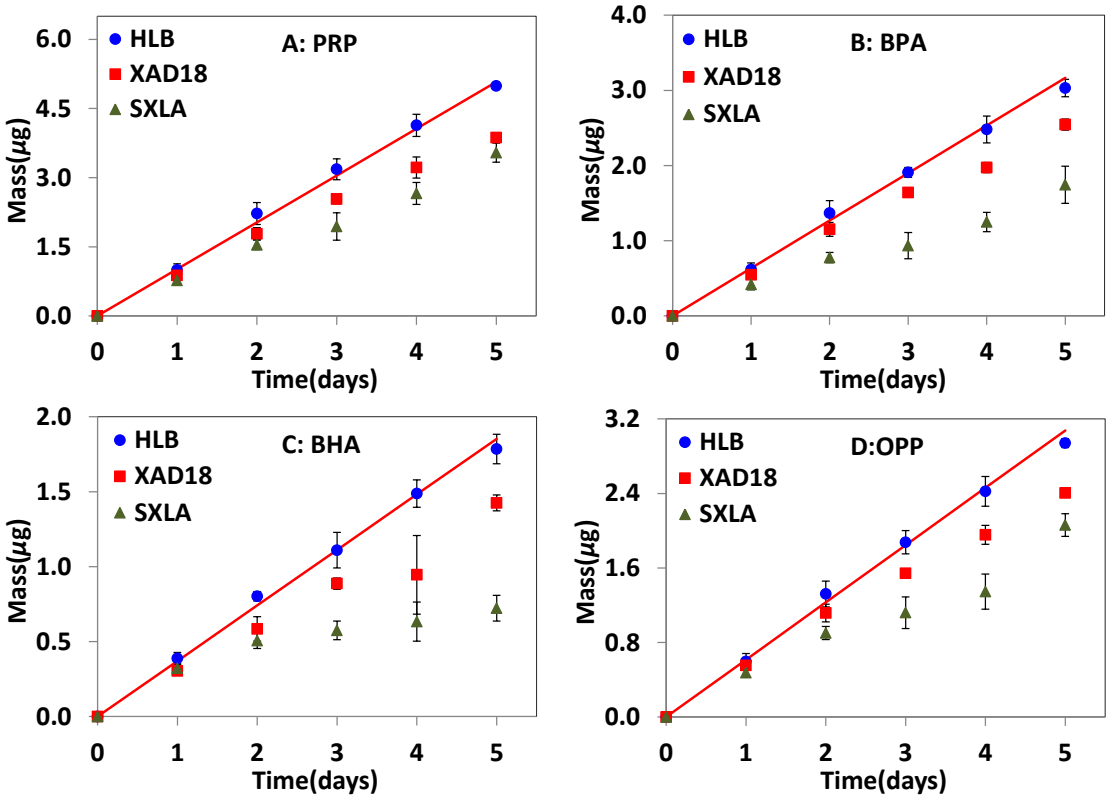


Figure 5: Measured masses (M, μg) of selected test chemicals in HLB, XAD18 and SXLA resin gels of DGT for different time (n=3). The solid lines are theoretical lines predicted by Equation (2). Error bars: 1 SD.

3.5 Field performance

HLB-DGT devices have been evaluated in a previous study,[14] which confirmed the HLB-DGT could be effective for routine monitoring of the test chemicals and provide reliable TWA concentrations of the test chemicals in wastewater. Thus, only DGT results were compared to evaluate the suitability of these three DGT applications in the field, although the 24-h composite auto-samples and grab-samples were also collected along with the DGT samples.

The results showed that all the 8 of 11 test chemicals (except IPRP, E2, EE2), were detectable from the influent by DGT samples, while only 5 of them (MEP, BPA, BHA, OPP and TCS) were found in the

effluent by DGT. No test chemicals were detected from the blank DGT samples. The detected chemicals could be always continuously accumulated by the DGT samplers from water with deployment time for 14 days in both the effluent and influent (**Figures 6a-f** and **S7**) confirmed the principle of DGT in field water sampling application.

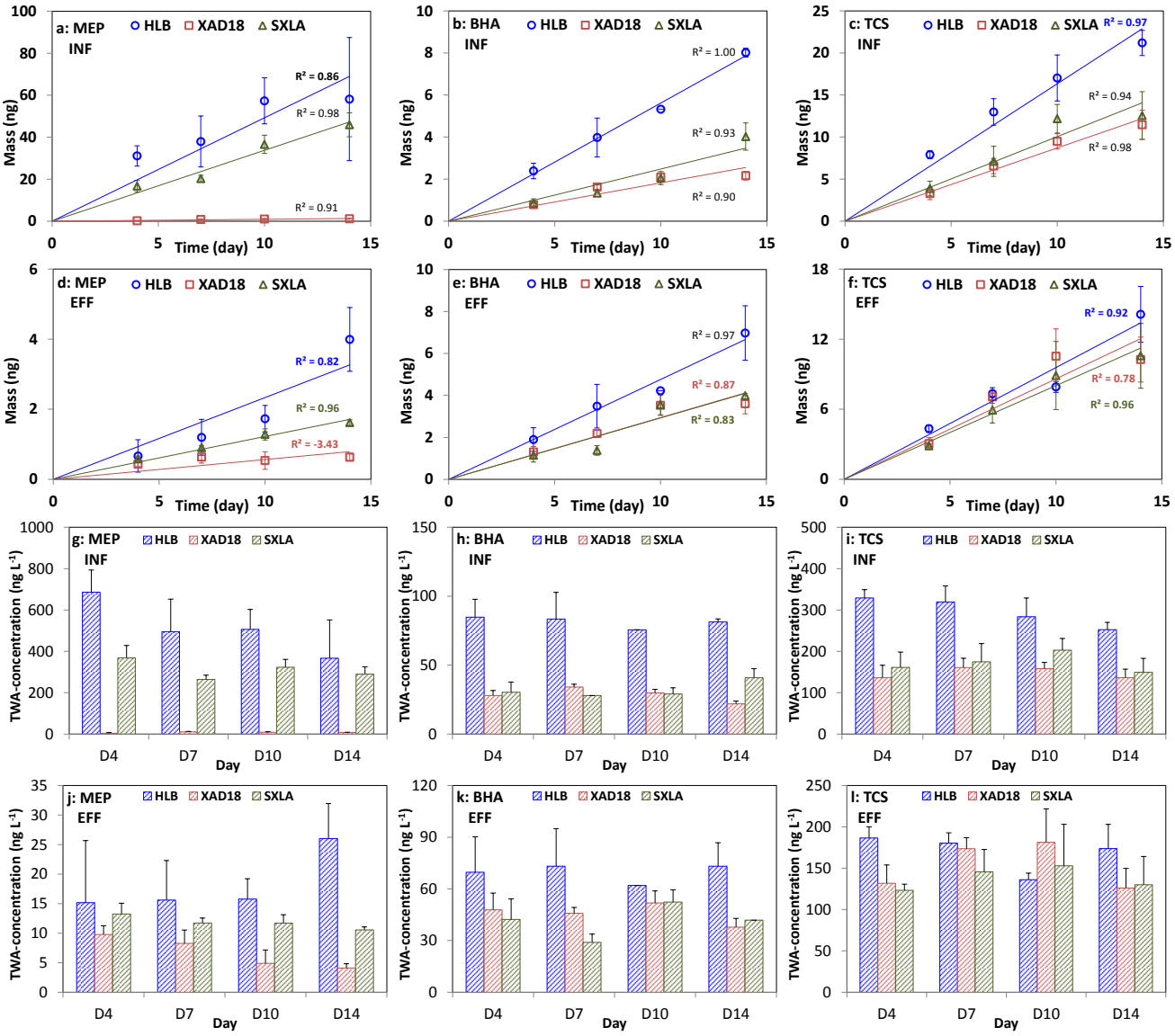


Figure 6: DGT uptake for selected test chemicals in influent (a-c) and effluent (d-f), and the TWA concentrations of these chemicals in influent (g-i) and effluent (j-l) from a UK WWTP for 14 days. Error bar: 1SD.

The results demonstrated the HLB-DGT could accumulate larger amounts of test chemicals for the whole

14 days duration of deployment than XAD18 and SXLA-DGT, which is consistent with the results of the laboratory time deployment and confirms that the XAD18 and SXLA-DGT could not be applied in the field directly. **Figure 6 g-l** showed that TWA concentrations for three types of DGT in the influent and effluent, larger differences were observed between HLB-DGT and XAD18/SXLA DGT in the influent than in the effluent. This difference could be due to the interferences from other chemicals, as the effluent contains much less interferences than influent after the treatment process, which reduces their effect on the performance of XAD18 and SXLA DGT devices.

4. CONCLUSION AND IMPLICATIONS

The HLB, XAD18 and SXLA resins were comparatively evaluated based on systematic tests of their uptake/sorption behaviours and performance of measurement for the 11 test chemicals (preservatives, oestrogens, antioxidants and disinfectants) under different environmental conditions in the laboratory as well as in a WWTP.

The XAD18 resin has the largest capacity for the majority of the test chemicals, the van der Waals and π-π interactions are the dominant interactions in controlling the sorption behaviour between test chemicals and resins. The performance test of three DGT devices was relatively independent of pH (3.5-8), ionic strengths (0.001 -0.1 M) and dissolve organic matter (0- 20 mg L^{-1}), but HLB and XAD18-DGT devices were more stable under different environmental conditions than SXLA-DGT. HLB-DGT can accumulate test chemicals consistently with theoretical predictions, indicating HLB-DGT can be directly and accurately applied for field measurement. Field application of three types of DGT was also conducted in a WWTP and the results confirmed the use of HLB-DGT sampler for *in situ* measurement of these test

chemicals. Thus, the selection of the suitable resins can be crucial for new DGT sampler development.

SUPPORTING INFORMATION

Information including experiment control, supplementary tables and figures was listed in the Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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Supporting Information for

Comparative evaluation of DGT samplers with different binding resins for *in situ* measurement of trace organic chemicals in waters

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CONTENTS

Supplementary Figures

Figure S1: Masses (μg) of test chemicals untaken by HLB, XAD18 and SXLA resin gels in 50 mL test chemical solutions of various concentration at pH=6 and 8 (IS= 0.01M, T= 20 ± 2 ℃; n=3); Error bars: 1SD;

Figure S2: Dynamic binding of test chemicals by HLB, XAD18 and SXLA resin gels in 20 mL solutions of 200 μg L^{-1} test chemicals (IS = 0.01 M and pH = 6.8 ± 0.1, T = 20 ± 2 ℃; n=3); Error bars: 1SD;

Figure S3: Effect of pH on DGT measurement with HLB, XAD18 and SXLA binding gels (IS = 0.01 M, T = 20 ± 2 ℃; n = 3). C_{DGT} are the test chemicals concentrations measured by DGT and C_b, their concentrations in the bulk solutions. The solid horizontal lines represent the value of 1 and the dotted horizontal lines represent the values at 0.9 and 1.1; Error bars: 1SD;

Figure S4: Effect of IS on DGT performance with HLB, XAD18 and SXLA binding gels (pH = 6.9 ± 0.2, T = 20 ± 2 ℃; n = 3). The solid horizontal lines represent the value of 1 and the dotted horizontal lines represent the values at 0.9 and 1.1; Error bars: 1SD;

Figure S5: Effect of DOM on DGT measurement with HLB, XAD18 and SXLA binding gels (pH = 6.9 ± 0.2, IS = 0.01 M, T = 20 ± 2 ℃; n = 3). The solid horizontal lines represent the value of 1 and the dotted horizontal lines represent the values at 0.9 and 1.1; Error bars: 1SD;

Figure S6: Measured masses (M, μg) of test chemicals in HLB, XAD18 and SXLA -DGTs deployed in well stirred solution for different time (IS = 0.01 M, pH = 6.8 ± 0.2, T= 24 ± 2 ℃; n=3). The solid lines are theoretical lines; Error bars: 1 SD;

Figure S7: Uptake of test chemicals in three types of DGT (n = 3) of influent and effluent of a UK WWTP for 14 days. Error bar: 1SD.

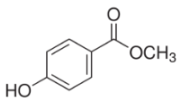
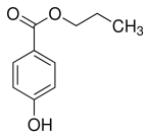
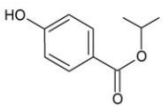
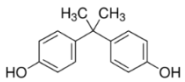
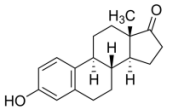
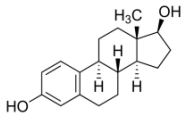
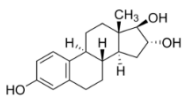
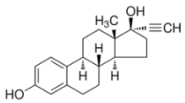
Lab experiment control description

New plastic-ware (including the DGT holders, water containers) was used for all experiments immersed and soaked in the methanol overnight and rinsed thoroughly in MQ water before use. All glassware was fully immersed and soaked in the Decon 90 solution (4 %) overnight and then rinsed thoroughly with tap water and MQ water, followed by baking at 450 ℃ for 4 hours (h) before use.

During the lab experiments, the pH was monitored both before and after the experiment (if the experiment time was less than 24 h) or daily (if the experiment time were more than 24 h) by a pH meter equipped with an Activon pH electrode (Radiometer Copenhagen, PHM93) to confirm the pH of water solution did not change more than 0.2 as adjusted, and the water temperature was measured every 8 h using a mercurial thermometer to ensure the temperature change was stayed within 2 ℃ as set. Solution pH was modified using NaAc and HCl for acidity or $NaHCO_3$ and NaOH for basicity. Ionic strength (IS) of the solution was adjusted using NaCl. Dissolved organic matter (DOM) concentration was changed by adding humic acid solution in the water solution. All experiments were undertaken in a cool and dark room and the water containers were covered by aluminium foil to prevent possible photo-degradation of test chemicals during the deployment period. During the period of experiments, 0.4 mL of tested water solution was sampled at the beginning, middle (or daily when take the DGT devices out) and end of the experiments to check for possible concentration changes in solution (similar sampling procedure were undertaken for all experiments unless stated specially). Blank and control experiments were conducted in every set of the experiment to prevent the possible contamination/change during the experiment, such as the degradation and adsorption to the tested materials or on the container wall/DGT devices. The DGT devices were deployed in the water at a stirring speed of 350 rpm by a magnetic stir bar. All the experiments were conducted in the solution with IS = 0.01 M and pH = 6.8 ± 0.1, T = 20 ± 2 ℃ unless stated specially.

All the laboratory experiment and field sampling were carried out at least triplicate unless stated specially, and the results were expresses as the average ± standard deviation (SD). The statistical analysis was conducted by IBM SPSS Statistics software (Version 22), the significance differences were statistically tested by analysis of variance (ANOVA) at 5 % significant level.

Table S1: Purity of standards and physical-chemical properties of 11 test chemicals[1].

Group	Chemical, purity and CAS No.	Structure	Molecular formula	Molecular weight	S_w / mgL^{-1} ($mmol\ L^{-1}$)	pKa	Log K_{OW}	SSA, PSA, ASA/$Å^2$	ASA:PSA	PA/$Å^2$	Aromatic bonds	H-Bond Donor/acceptor
Preservative	Methylparaben ≥99.0 % P99-76-3		$C_8H_8O_3$	152.15	2500 (16.43)	8.31	2	349 47 303	6.5	23-53	6	1/4
	Propylparaben ≥99.0 % 94-13-3		$C_{10}H_{12}O_3$	180.2	500 (2.77)	8.23	2.98	414 47 368	7.9	30-60	6	1/4
	Isopropylparaben ≥99.0 % 4191-73-5		$C_{10}H_{12}O_3$	180.2	689.7 (3.83)	8.4	2.91	408 47 361	7.8	29-60	6	1/4
Oestrogen	Bisphenol-A ≥99.0 % 1980-5-7		$C_{15}H_{16}O_2$	228.29	120 (0.53)	9.94/ 11.97	3.64	416 40 375	9.3	42-66	12	2/4
	Estrone ≥99.0 % 53-16-7		$C_{18}H_{22}O_2$	270.37	30 (0.11)	10.33	3.43	396 37 359	9.6	42-83	6	2/4
	β-estradiol ≥98.0 % 50-28-2		$C_{18}H_{24}O_2$	272.39	3.9 (0.014)	10.33	3.94	393 40 352	8.7	34-85	6	1/4
	Estriol ≥99.0 % 50-27-1		$C_{18}H_{24}O_3$	288.39	440.8 (1.53)	10.33/ 13.62	2.81	398 61 337	5.6	38-88	6	2/4
	17*α*-Ethinylestradiol ≥98.0 % 57-63-6		$C_{20}H_{24}O_2$	296.41	11.3 (0.038)	10.33	4.12	408 40 368	9.1	40-90	6	3/6

[1] This table is continued onto the next page.

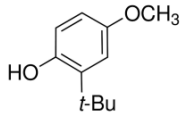
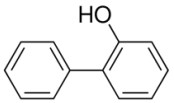
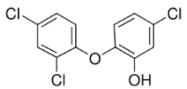
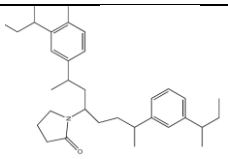
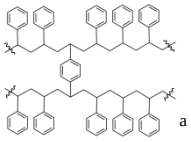
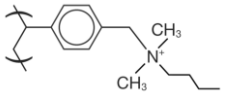
Antioxidant	Butylated hydroxyanisole ≥98.5 % 1948-33-0		$C_{11}H_{16}O_2$	180.24	212.8 (1.18)	10.55	3.5	394 29 365	12.4	36-59	6	2/4
Disinfectant	Ortho-phenylphenol ≥99.0% 90-43-7		$C_{12}H_{10}O$	170.21	700 (4.11)	9.65	3.28	346 20 326	16.1	29-57	12	1/2
	Triclosan ≥97% 3380-34-5		$C_{12}H_7Cl_3O_2$	289.55	10 (0.035)	7.68	4.66	413 29 384	13.0	40-71	12	1/2

Table S2: Physical-chemical properties of three resins.

Resin type	HLB	XAD18	SXLA
Structure		 a	
Sorbent substrate	Copolymer	Macroreticular cross-linked aromatic polymer	Polymer-based
Adsorption mode	Reversed-phase	–	Strong Anion Mixed
pH stability	1-14	1-14	1-14
Specific surface area (m^2 g^{-1})	727-889 (771)	≥800	520
Average particle diameter (μm)	50-65 (56)	425 ±50 (63-150)[b]	100

a: General structure of a styrene DVB copolymer adsorbent, which is similar with XAD18 (the exact structure of XAD18 was not informed by the DOW company as the trade secret)
b: After grinded

86 **Table S3:** Parameters of Langmuir, Freundlich and Redlich-Peterson models for test chemical sorption[2].

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Chemical	pH	Resin	Langmuir			Freundlich[a]			Redlich-Peterson[b]			
			K_L / L mmol^{-1}	Q_{max}/ mmol kg^{-1}	R^2	K	n	R^2	K	α	β	R^2
MEP	6	HLB	92	13.0	0.98	47.8	2.15	1.00	6689	164	0.59	1.00
		XAD18	32	17.5	0.96	69.5	1.65	0.99	--			
		SXLA	339	4.8	0.90	12.6	3.37	0.99	17453	1514	0.73	0.99
	8	HLB	1086	3.5	0.94	7.2	4.86	0.95	7624	1424	0.88	1.00
		XAD18	179	8.9	0.93	26.1	2.77	0.99	15679	669	0.68	0.99
		SXLA	300	5.9	0.94	15.0	3.35	0.98	6976	595	0.78	0.99
PRP	6	HLB	145	31.0	0.97	119.1	2.30	0.99	27643	279	0.62	1.00
		XAD18	169	32.8	0.96	125.6	2.37	0.99	36702	351	0.63	0.99
		SXLA	576	18.0	0.96	49.3	3.45	0.96	24612	761	0.83	0.99
	8	HLB	1018	14.0	1.00	30.3	4.48	0.83	13661	1015	1.01	1.00
		XAD18	825	22.7	0.99	57.7	3.76	0.92	28951	917	0.91	1.00
		SXLA	502	17.6	0.95	46.1	3.50	0.96	28798	871	0.81	0.99
IPRP	6	HLB	200	19.1	0.97	77.1	2.40	0.99	19697	325	0.65	1.00
		XAD18	194	21.9	0.95	89.9	2.38	0.99	56198	695	0.61	0.99
		SXLA	981	10.4	0.96	28.7	3.79	0.96	25943	1364	0.84	1.00
	8	HLB	1485	8.9	1.00	19.9	4.70	0.83	12861	1481	1.01	1.00
		XAD18	1593	14.1	1.00	34.5	4.33	0.88	26418	1630	0.96	1.00
		SXLA	1136	9.6	0.95	25.0	4.02	0.95	27077	1610	0.86	0.99
BPA	6	HLB	184	37.6	0.98	240.0	1.93	0.98	15844	114	0.64	0.99
		XAD18	289	33.7	0.97	185.5	2.19	0.98	19205	204	0.73	0.99
		SXLA	576	23.6	0.99	88.1	2.86	0.94	16334	520	0.93	0.99
	8	HLB	533	26.1	0.98	101.1	2.73	0.94	15909	474	0.93	0.98
		XAD18	815	30.2	0.96	122.9	2.79	0.93	32117	661	0.88	0.96
		SXLA	555	24.2	0.99	88.0	2.86	0.95	17727	494	0.90	0.99
E1	6	HLB	1216	9.8	0.95	65.5	2.65	0.90	8154	5230	1.35	0.96
		XAD18	1613	13.1	0.81	104.8	2.56	0.76	16241	5009	1.25	0.82
		SXLA	2213	10.3	0.84	38.0	3.88	0.79	14496	10764	1.37	0.87
	8	HLB	1711	10.7	0.91	52.1	3.18	0.90	23649	1291	0.90	0.91
		XAD18	1206	16.4	0.92	166.1	2.27	0.92	44371	513	0.69	0.92
		SXLA	1385	12.4	0.91	82.0	2.70	0.92	32015	797	0.77	0.92
E2	6	HLB	774	10.9	0.95	88.2	2.26	0.85	6591	2784	1.31	0.97
		XAD18	776	17.6	0.89	267.8	1.86	0.84	12133	2240	1.22	0.90
		SXLA	1247	11.7	0.89	79.7	2.55	0.76	11327	5237	1.32	0.92
	8	HLB	868	12.6	0.94	138.0	2.08	0.88	10051	1344	1.10	0.94
		XAD18	1225	19.2	0.97	306.0	1.99	0.96	27867	666	0.86	0.97
		SXLA	963	13.0	0.93	137.4	2.13	0.86	11120	1915	1.15	0.93

[2] This table is continued onto the next page.

Chemical	pH	Resin	Langmuir			Freundlich[a]			Redlich-Peterson[b]			
			K_{L} / L mmol^{-1}	Q_{max}/ mmol kg^{-1}	R^2	K	n	R^2	K	α	β	R^2
E3	6	HLB	529	4.9	0.96	26.0	2.55	1.00	18074	869	0.66	1.00
		XAD18	760	9.5	0.98	63.7	2.41	0.98	17202	536	0.74	0.99
		SXLA	2844	3.8	0.99	12.5	3.98	0.92	16081	2823	0.92	1.00
	8	HLB	3877	2.4	0.99	6.1	5.04	0.79	8165	3981	1.03	0.99
		XAD18	1956	9.3	0.98	44.3	3.05	0.93	21855	1668	0.93	0.99
		SXLA	529	4.9	0.96	9.3	4.51	0.90	19056	4113	0.92	0.99
EE2	6	HLB	439	22.4	0.93	400.8	1.65	0.88	8085	6399	1.55	0.94
		XAD18	816	24.9	0.91	478.6	1.78	0.89	19490	1120	1.06	0.91
		SXLA	1149	18.8	0.92	166.5	2.36	0.91	26110	714	0.88	0.92
	8	HLB	964	17.7	0.94	193.6	2.15	0.96	107461	670	0.57	0.96
		XAD18	1400	20.2	0.92	265.1	2.14	0.94	--[d]			
		SXLA	1242	17.3	0.95	154.9	2.37	0.95	35525	588	0.77	0.95
BHA	6	HLB	215	31.9	0.97	206.5	1.98	0.99	20101	150	0.62	0.99
		XAD18	234	35.4	0.97	249.2	1.95	0.98	24856	154	0.61	0.99
		SXLA	507	25.3	0.97	119.8	2.53	0.97	25067	416	0.78	0.99
	8	HLB	618	22.7	0.98	98.0	2.66	0.95	18917	502	0.87	0.98
		XAD18	1159	30.1	0.98	133.8	2.84	0.95	37808	1009	0.95	0.98
		SXLA	666	23.9	0.97	94.8	2.85	0.97	32428	592	0.79	0.99
OPP	6	HLB	135	46.1	0.98	377.8	1.68	0.99	12101	59	0.60	0.99
		XAD18	153	42.2	0.98	312.6	1.78	0.98	15612	81	0.59	0.99
		SXLA	290	31.2	0.98	172.0	2.17	0.97	12146	203	0.83	0.99
	8	HLB	379	29.0	0.98	146.1	2.31	0.95	12500	304	0.91	0.98
		XAD18	463	33.8	0.97	186.8	2.28	0.95	17093	379	0.93	0.97
		SXLA	330	29.1	0.98	149.5	2.26	0.97	12691	237	0.84	0.99
TCS	6	HLB	--[c]			380.7	1.79	0.94	14059	7925	1.39	0.96
		XAD18	--			1041.6	1.48	0.96	21470	160	0.71	0.96
		SXLA	--			1031.8	1.50	0.92	23914	223	0.75	0.97
	8	HLB	--			213.6	2.09	0.92	19919	4142	1.17	0.94
		XAD18	--			--[d]			--			
		SXLA	--			136.1	2.36	0.91	21760	3320	1.10	0.93

a: The Freundlich model was expressed as: $q_e = K \cdot C_w^{1/n}$;[1]

b: The Redlich-Peterson model was expressed as: $q_e = \frac{K \cdot C_w}{1 + \alpha \cdot C_w^{\beta}}$;[2]

c: Fail to good fitting for Langmuir model because of the linear sorption

d: Fail to good fitting for Freundlich and Redlich-Peterson models

Table S4: Estimated capacities of three resin gels (Q, μg/gel) and maximum water concentrations (μg L^{-1}) for typical deployment time.

Test	HLB-DGT			XAD18-DGT			SXLA-DGT		
Chemicals	Q[a]	2 weeks[b]	1 month	Q	2 weeks	1 month	Q	2 weeks	1 month
MEP	17.0	65	31	28.7	110	52	23.4	90	42
PRP	129.2	575	268	162.4	722	337	166.1	739	345
IPRP	51.3	229	107	55.4	247	115	60.0	267	125
BPA	150.5	826	385	139.5	765	357	136.1	746	348
E1	71.6	393	183	90.6	497	232	75.2	413	193
E2	95.0	699	326	113.3	833	389	102.0	750	350
E3	22.8	131	61	46.5	267	124	36.0	207	96
EE2	96.4	747	348	94.2	730	341	102.4	793	370
BHA	196.4	1217	568	206.8	1281	598	218.9	1356	633
OPP	167.3	850	397	167.8	853	398	180.0	915	427
TCS	97.0	703	328	120.4	873	407	92.1	668	312

a: Capacity of each test chemicals was calculated based on the amounts of resin in each gel (ca. 32mg) and smaller Q_{max} in two pH system, the capacity of TCS was used the experiment data directly due to the failure of Langmuir modelling;

b: Maximum water concentrations for test chemicals were estimated for 2 weeks or 1 months deployment in water at 25 ℃.

Table S5: Parameters of pseudo-first-order and pseudo-second-order sorption kinetic models[a].

Test Chemical	Resin	pseudo-first-order[b]	pseudo-second-order		Weber-Morris	
		R^2	k	R^2	K_a	R^2
MEP	HLB	0.59	0.103	1.00	0.0033	0.85
	XAD18	0.75	0.056	0.98	0.0029	0.94
	SXLA	0.65	0.089	0.99	0.0003	0.89
PRP	HLB	0.52	0.081	0.99	0.0035	0.77
	XAD18	0.36	0.274	1.00	0.0030	0.63
	SXLA	0.73	0.034	0.99	0.0040	0.93
BPA	HLB	0.55	0.106	1.00	0.0034	0.81
	XAD18	0.36	0.337	1.00	0.0027	0.64
	SXLA	0.61	0.067	1.00	0.0038	0.86
E1	HLB	0.62	0.068	1.00	0.0036	0.86
	XAD18	0.58	0.143	1.00	0.0026	0.90
	SXLA	0.82	0.054	0.96	0.0027	0.98
E2	HLB	0.63	0.069	1.00	0.0035	0.87
	XAD18	0.57	0.151	1.00	0.0028	0.87
	SXLA	0.85	0.047	0.95	0.0029	0.99
E3	HLB	0.58	0.113	1.00	0.0033	0.84
	XAD18	0.48	0.218	1.00	0.0024	0.84
	SXLA	0.84	0.045	0.96	0.0032	0.99
EE2	HLB	0.53	0.156	1.00	0.0029	0.83
	XAD18	0.48	0.204	1.00	0.0027	0.79
	SXLA	0.78	0.061	0.97	0.0030	0.97
BHA	HLB	0.67	0.074	0.99	0.0034	0.91
	XAD18	0.47	0.229	1.00	0.0022	0.85
	SXLA	0.79	0.064	0.97	0.0028	0.97
OPP	HLB	0.64	0.097	0.99	0.0031	0.90
	XAD18	0.44	0.268	1.00	0.0024	0.80
	SXLA	0.82	0.045	0.96	0.0033	0.98
TCS	HLB	0.50	0.117	1.00	0.0035	0.77
	XAD18	0.25	0.664	1.00	0.0024	0.46
	SXLA	0.59	0.069	1.00	0.0039	0.84

a: Equation for pseudo-first-order model: $\log(q_e - q_t) = \log(q_e) - \frac{k \cdot t}{2.303}$;[3] Equation for pseudo-second-order model: $\frac{t}{q_t} = \frac{1}{k \cdot q_e^2} + \frac{t}{q_e}$[3] and the Weber-Morris model: $q_t = A + K_a \cdot t^{0.5}$;[4]

b: The pseudo-first-order rate constant was not listed due to the poor correlation coefficient, R^2

111 **Table S6:** Overall recoveries (%) and separate recoveries (%) of test chemical extraction for three types of
112 binding gels at 100, 250 and 500 μg L^{-1} solution (n=4 for each concentration of each binding gel, n=36 in
113 total).

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Gel		MEP	E3	IPRP	PRP	BPA	E2	EE2	OPP	E1	BHA	TCS
Overall	Average	121	101	119	118	99.1	87.7	110	65.9	71.4	65.9	86.6
	SD	9.2	17.1	10.7	11.3	6.7	7.2	16.0	6.6	8.1	6.6	12.0
HLB	Average	122	103	123	122	102	87.6	112	96.1	72.2	64.6	87.9
Overall	SD	5.6	12.4	11.1	10.8	6.2	7.5	18.3	5.3	8.3	5.0	11.6
HLB	Average	122	117	122	116	100	80.4	136	96.1	81.1	62.1	98.7
100 μg L^{-1}	SD	2.8	5.6	20.4	16.8	2.1	2.9	8.6	6.1	6.7	4.6	6.9
HLB	Average	125	101	122	129	110	94.0	101	99.7	70.6	66.0	90.8
250 μg L^{-1}	SD	8.4	7.5	3.4	4.3	4.0	7.9	3.8	5.4	3.9	7.3	5.0
HLB	Average	117	90.9	126	122	97.3	88.4	99.6	92.4	64.9	65.7	74.3
500 μg L^{-1}	SD	1.7	3.2	2.7	5.1	3.4	3.3	4.3	1.5	3.0	2.7	2.6
SXLA	Average	118	91.6	114	114	95.4	836.	107	92.	69.3	64.2	85.3
Overall	SD	12.2	13.8	9.8	9.9	7.2	7.5	13.6	5.9	9.1	6.9	12.8
SXLA	Average	104	107	108	116	90.2	79.2	121	93.4	80.0	62.7	98.4
100 μg L^{-1}	SD	7.2	11.8	14.8	14.4	3.5	7.4	10.3	5.5	4.1	4.9	3.0
SXLA	Average	131	84.9	114	119	104	88.8	106	95.4	68.4	68.0	86.7
250 μg L^{-1}	SD	3.5	8.6	6.9	5.3	3.9	4.8	8.0	5.5	1.2	9.3	4.7
SXLA	Average	121	82.9	118	107	92.6	82.8	94.4	87.2	59.6	61.9	70.7
500 μg L^{-1}	SD	1.3	2.4	3.2	4.4	5.1	8.1	5.4	4.5	3.0	6.1	7.8
XAD18	Average	122	109	122	119	99.6	92.1	111	97.2	72.6	69.0	86.5
Overall	SD	8.8	20.6	9.3	12.3	5.1	3.9	16.8	5.8	7.2	7.0	12.4
XAD18	Average	115	132	117	118	95.9	91.8	129	104	81.4	71.5	98.2
100 μg L^{-1}	SD	3.7	16.4	14.1	13.6	3.4	4.7	8.4	3.9	1.6	9.4	3.6
XAD18	Average	126	101	120	127	103	91.7	110	94.2	70.7	68.7	90.1
250 μg L^{-1}	SD	7.9	11.6	4.5	13.0	4.5	3.8	9.7	3.8	3.9	8.4	2.4
XAD18	Average	126	92.8	128	112.3	99.8	92.7	93.9	94.0	65.7	66.7	71.2
500 μg L^{-1}	SD	10.2	2.7	4.2	7.1	5.2	4.3	7.9	4.0	1.8	2.5	5.2

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Table S7: Average C_{DGT}/C_b for three types of DGT under pH=3.5-9.5 (n=18).

Resin	Statistics	MEP	PRP	IPRP	BPA	E1	E2	E3	EE2	BHA	OPP	TCS
HLB	Average	1.00	0.99	0.99	1.01	0.97	1.08	1.04	1.06	0.98	1.03	0.85
	SD	0.07	0.06	0.06	0.07	0.07	0.06	0.12	0.09	0.07	0.06	0.19
XAD18	Average	0.80	1.04	1.04	1.09	1.02	1.15	1.13	1.15	1.05	1.10	0.89
	SD	0.08	0.07	0.07	0.06	0.08	0.08	0.16	0.10	0.10	0.05	0.18
SXLA	Average	0.91	0.91	0.91	0.91	0.87	1.00	0.96	0.97	0.92	0.97	0.56
	SD	0.12	0.14	0.13	0.14	0.16	0.13	0.17	0.18	0.11	0.14	0.14

Table S8: Average ratios of C_{DGT}/C_b for three types of DGT under different IS conditions (n=12).

Resin	Statistics	MEP	PRP	IPRP	BPA	E1	E2	E3	EE2	BHA	OPP	TCS
HLB	Average	1.00	0.99	0.99	1.01	0.97	1.08	1.04	1.06	0.98	1.03	0.85
	SD	0.07	0.06	0.06	0.07	0.07	0.06	0.12	0.09	0.07	0.06	0.19
XAD18	Average	0.80	1.04	1.04	1.09	1.02	1.15	1.13	1.15	1.05	1.10	0.89
	SD	0.08	0.07	0.07	0.06	0.08	0.08	0.16	0.10	0.10	0.05	0.18
SXLA	Average	0.91	0.91	0.91	0.91	0.87	1.00	0.96	0.97	0.92	0.97	0.56
	SD	0.12	0.14	0.13	0.14	0.16	0.13	0.17	0.18	0.11	0.14	0.14

Table S9: Average ratios of C_{DGT}/C_b for three types of DGT under different DOM concentrations (n=15).

Resin	Statistics	MEP	PRP	IPRP	BPA	E1	E2	E3	EE2	BHA	OPP	TCS
HLB	Average	1.03	1.01	1.00	1.06	1.00	1.09	0.99	1.13	0.97	1.05	0.74
	SD	0.03	0.04	0.04	0.04	0.05	0.05	0.05	0.06	0.04	0.05	0.03
XAD18	Average	0.72	0.96	0.99	1.09	1.04	1.09	0.99	1.15	0.88	1.04	0.71
	SD	0.04	0.08	0.08	0.09	0.09	0.08	0.07	0.11	0.04	0.08	0.05
SXLA	Average	0.91	0.98	0.94	0.90	0.87	1.07	0.84	1.03	0.84	1.01	0.57
	SD	0.06	0.06	0.06	0.07	0.08	0.07	0.08	0.09	0.08	0.06	0.10

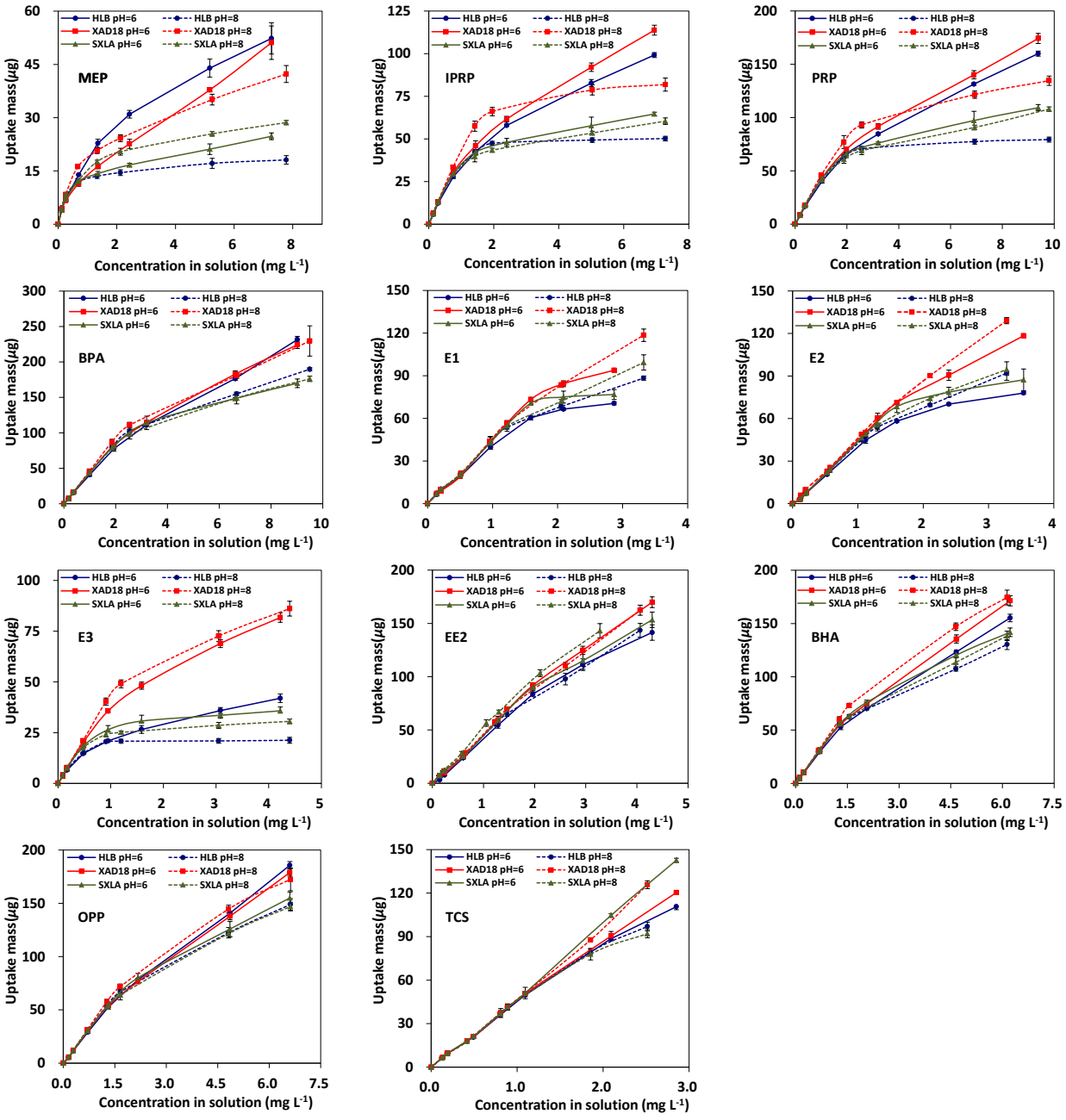
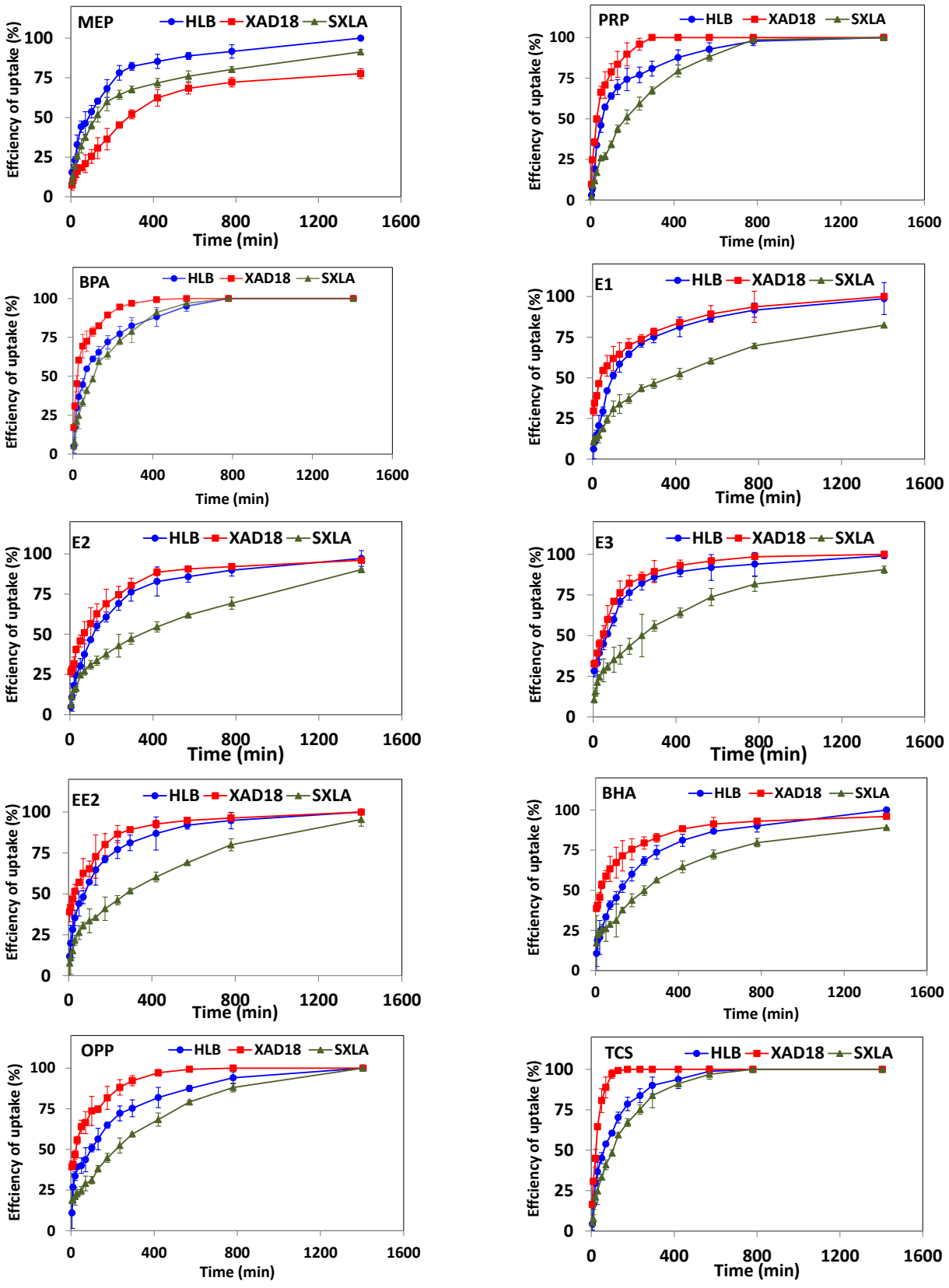


Figure S1: Masses (μg) of test chemicals uptaken by HLB, XAD18 and SXLA resin gels in 50 mL test chemical solutions of various concentration at pH=6 and 8 (IS= 0.01M, T= 20 ±2 ℃; n=3); Error bars: 1SD.



135
136 **Figure S2:** Dynamic binding of test chemicals by HLB, XAD18 and SXLA resin gels in 20 mL solutions of
137 200 μg L^{-1} test chemicals (IS = 0.01 M and pH = 6.8 ± 0.1, T = 20 ± 2 ℃; n=3); Error bars: 1SD.

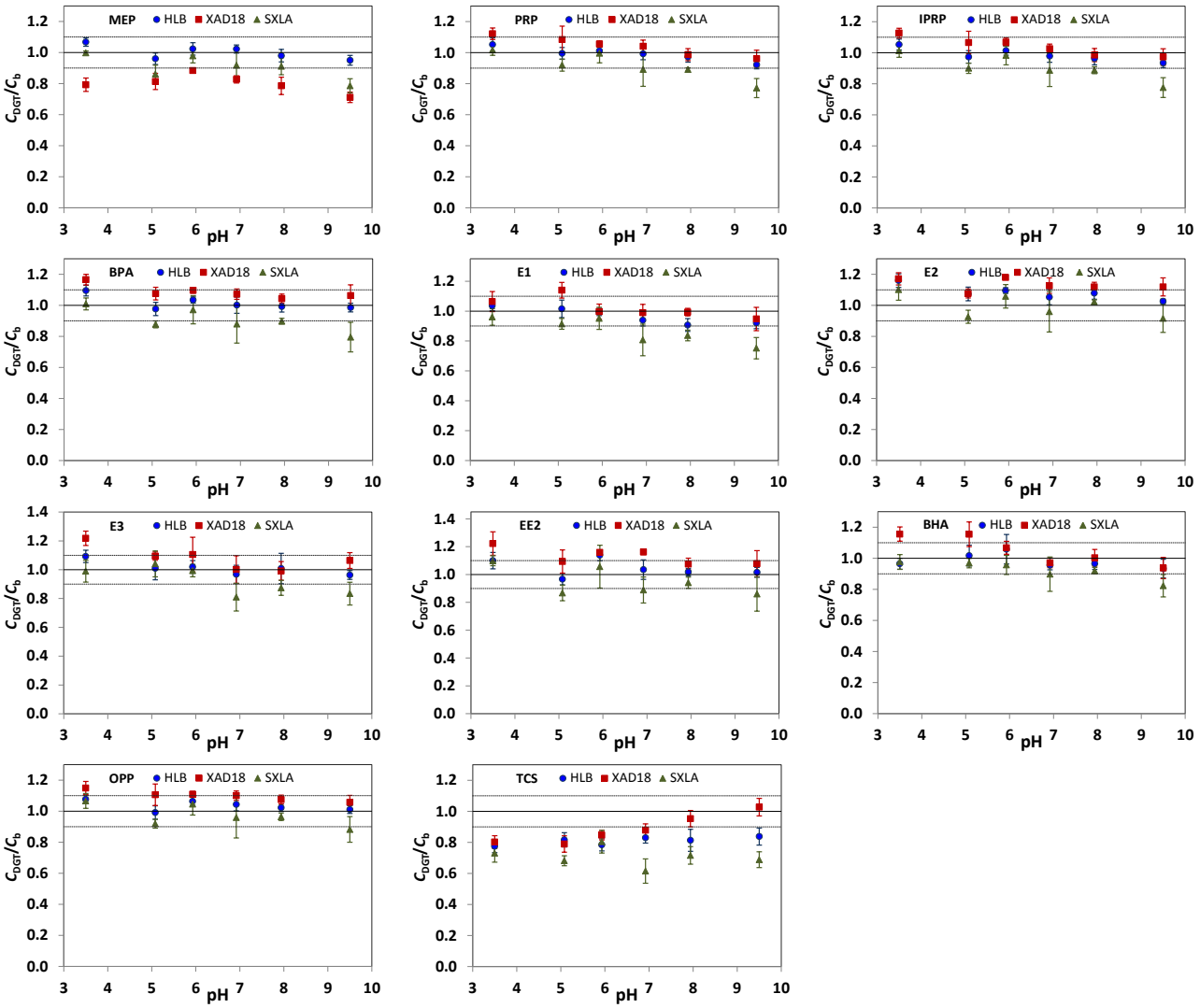


Figure S3: Effect of pH on DGT measurement with HLB, XAD18 and SXLA binding gels (IS = 0.01 M, T = 20 ± 2 ℃; n = 3). C_{DGT} are the test chemicals concentrations measured by DGT and C_b, their concentrations in the bulk solutions. The solid horizontal lines represent the value of 1 and the dotted horizontal lines represent the values at 0.9 and 1.1; Error bars: 1SD

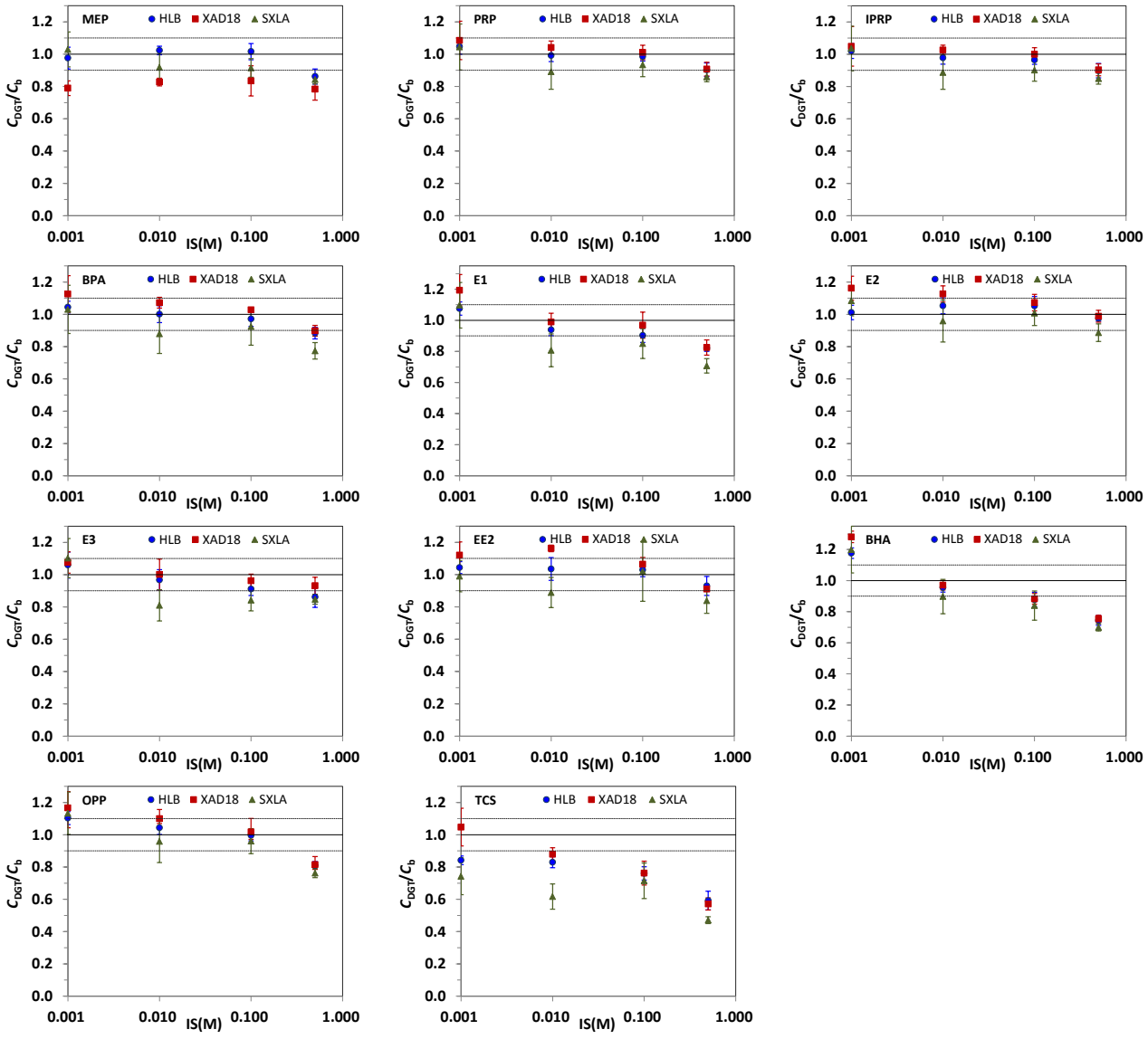


Figure S4: Effect of IS on DGT performance with HLB, XAD18 and SXLA binding gels (pH = 6.9 ± 0.2, *T* = 20 ± 2 ℃; n = 3). The solid horizontal lines represent the value of 1 and the dotted horizontal lines represent the values at 0.9 and 1.1; Error bars: 1SD.

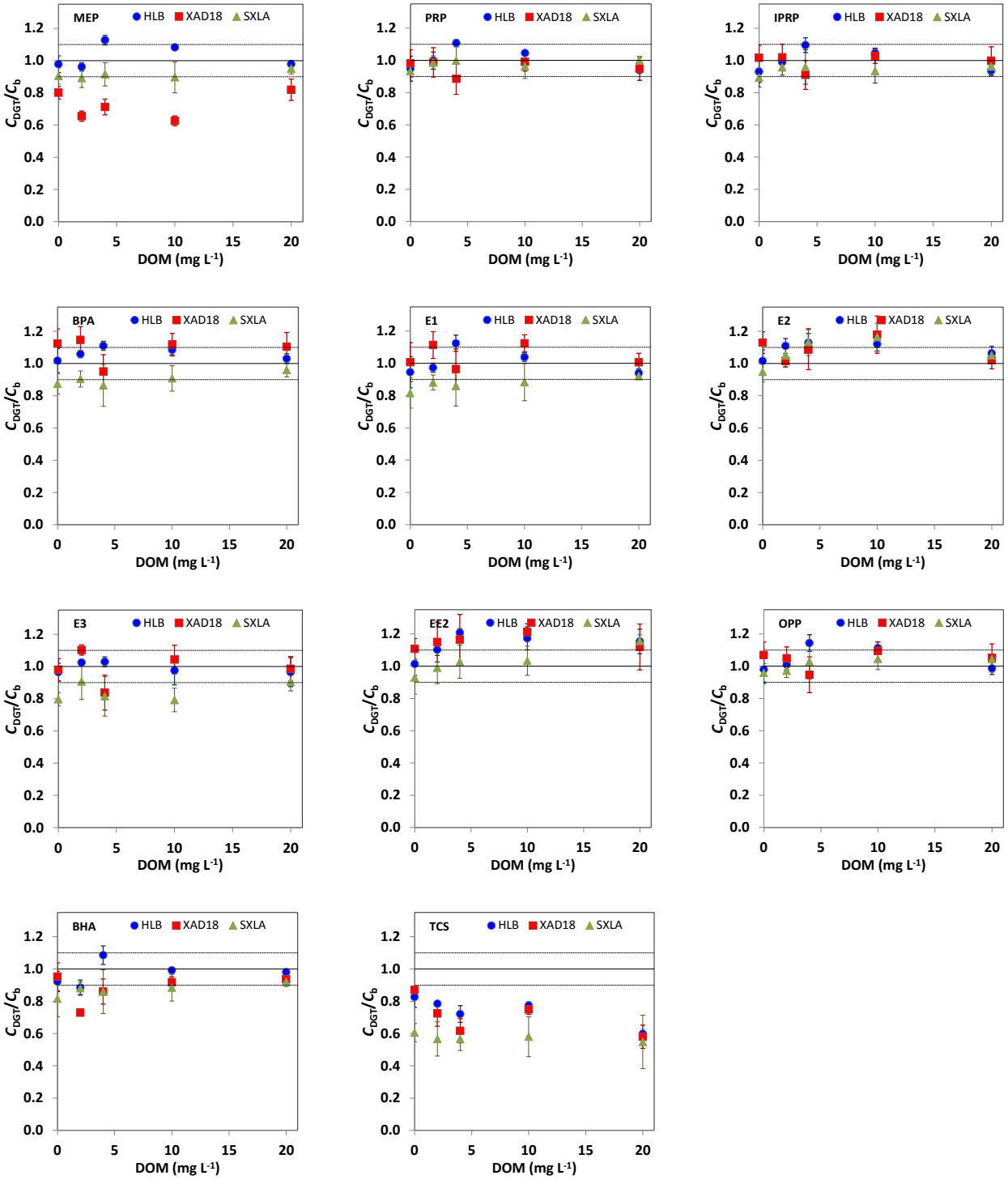


Figure S5: Effect of DOM on DGT measurement with HLB, XAD18 and SXLA binding gels (pH = 6.9 ± 0.2, IS = 0.01 M, T = 20 ± 2 ℃; n = 3). The solid horizontal lines represent the value of 1 and the dotted horizontal lines represent the values at 0.9 and 1.1; Error bars: 1SD.

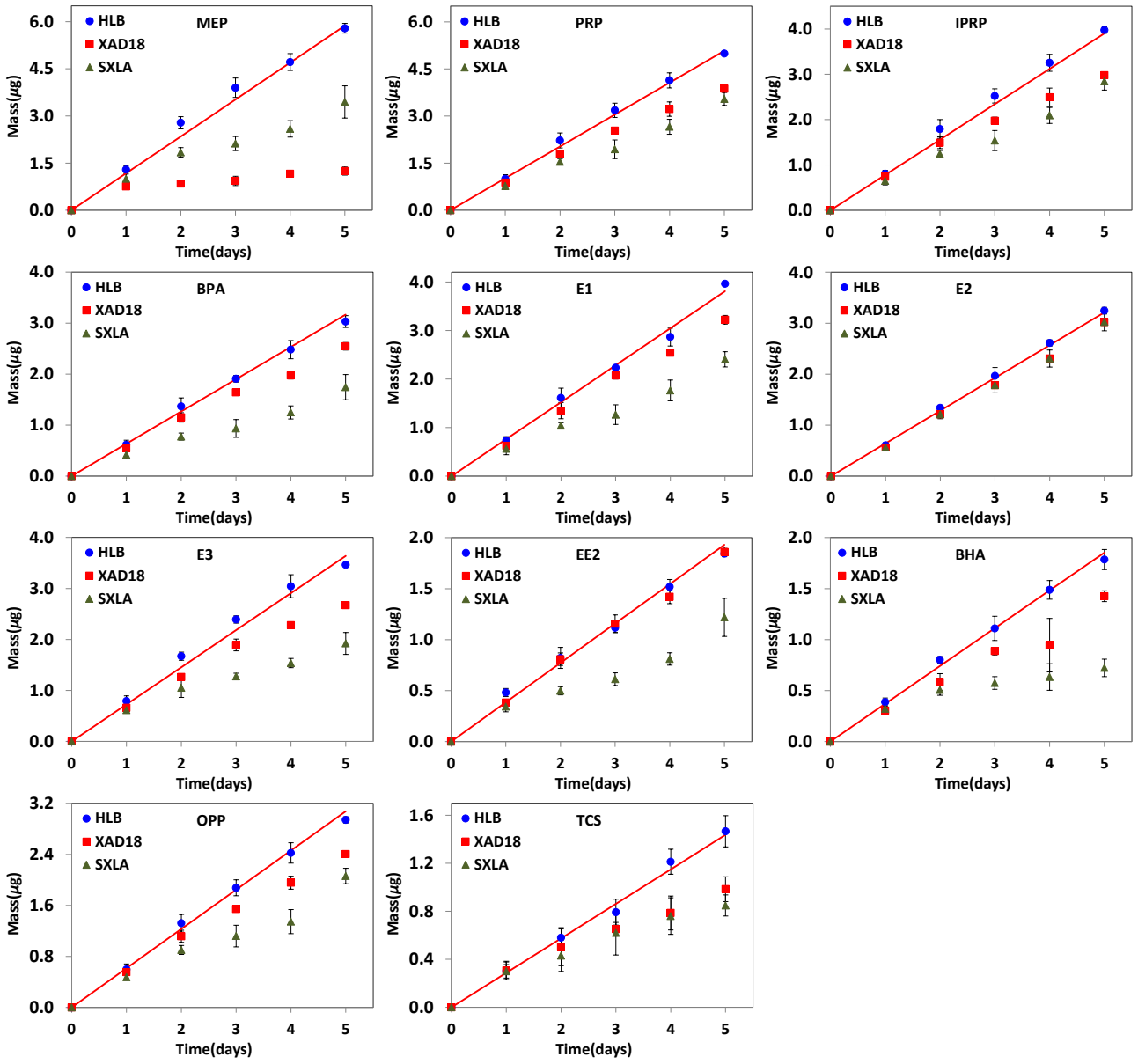


Figure S6: Measured masses (M, μg) of test chemicals in HLB, XAD18 and SXLA -DGT deployed in well stirred solution for different time (IS = 0.01 M, pH = 6.8 $\pm$ 0.2, T= 24 $\pm$ 2 ℃; n=3). The solid lines are theoretical lines; Error bars: 1 SD.

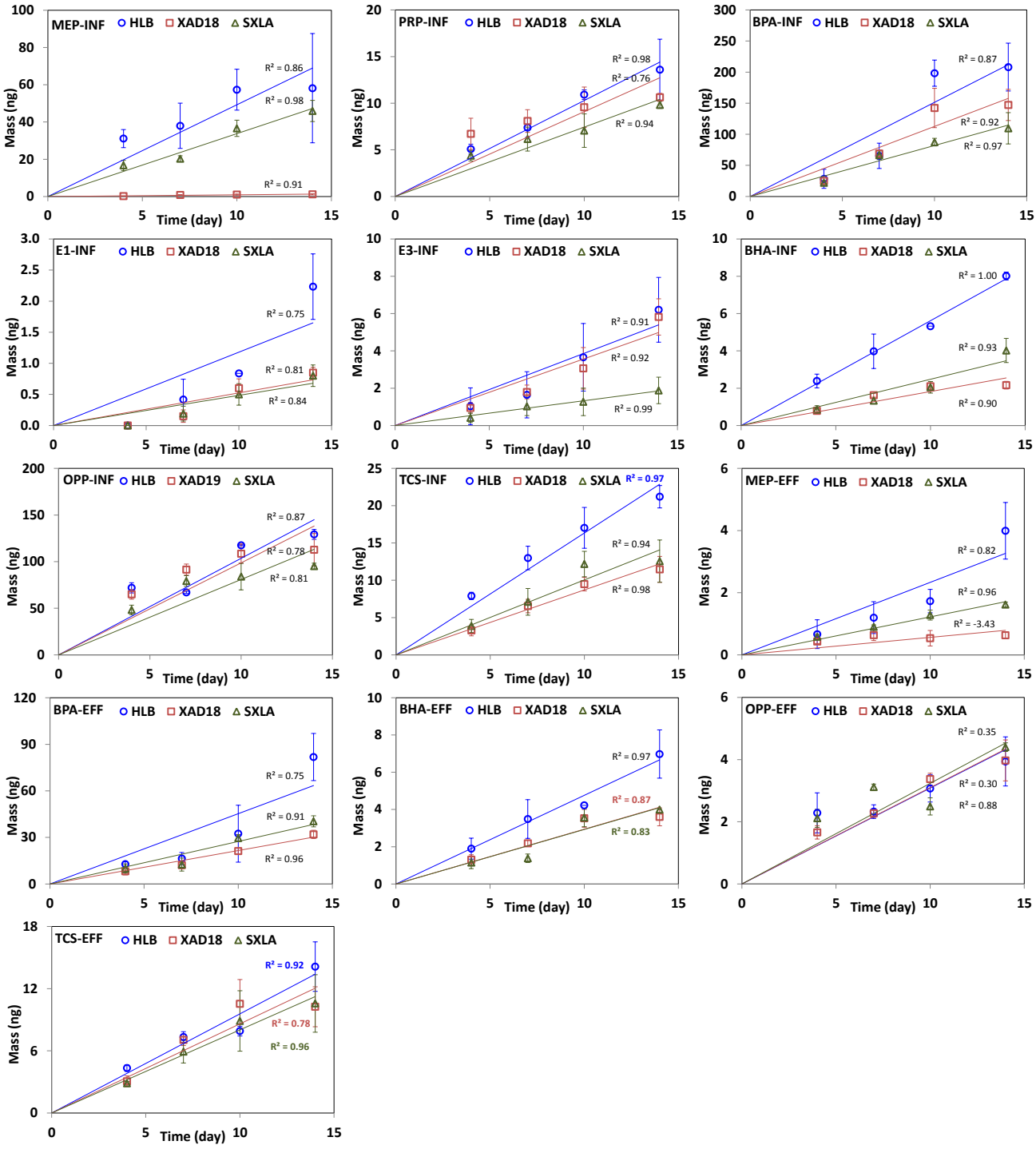


Figure S7: Uptake of test chemicals in three kinds of DGT (n = 3) of influent and effluent of a UK WWTP for 14 days. Error bar: 1SD.

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Paper III

Simultaneous Determination of 20 Trace Organic Chemicals in Waters by Solid-phase Extraction (SPE) with Triple-quadrupole MS (QqQ-MS) and Hybrid Quadrupole Orbitrap High Resolution MS (Q-Orbitrap-HRMS)

Simultaneous determination of 20 trace organic chemicals in waters by solid phase extraction (SPE) with triple-quadrupole MS (QqQ-MS) and hybrid quadrupole Orbitrap high resolution MS (Q-Orbitrap-HRMS)

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Abstract

A sensitive method for simultaneous determination of 20 trace organic chemicals (TOrCs, including preservatives, antioxidants, disinfectants, oestrogens and alkyl-phenols) in surface water and wastewater has been developed and validated based on the optimisation of solid-phase extraction (SPE) followed by liquid chromatography-mass spectrometry (LC-MS) analysis. 500 mL acidified (pH = 2.5) water samples were pre-concentrated by Supel-Select HLB cartridge (200 mg, 6 mL) and eluted with 10 mL mixture of acetonitrile and ethyl acetate (50:50, v/v). This optimised SPE procedure could provide > 75 % recoveries for the majority of TOrCs. The instrumental methods were developed using two different LC-MS systems: a triple-quadrupole MS (QqQ-MS) and a hybrid quadrupole Orbitrap high resolution MS (Q-Orbitrap-HRMS), both showed good performance, but the former system provided better linearity and method precision, with the latter system providing 2-33 times lower detection limits. Different matrix effects were observed for both systems: No remarkable matrix effects were observed for Q-Orbitrap-HRMS but significant matrix effects were found in influent and river water samples for the QqQ-MS. This analytical method was subsequently successfully employed to analyse the river waters and wastewaters from China, which confirmed its applicability to environmental samples.

Keywords

Trace organic chemicals (TOrCs), Surface water, Wastewater, Liquid chromatography-tandem mass spectrometry (LC-MS/MS), Liquid chromatography-high resolution MS (LC-HRMS)

1. Introduction

Preservatives, antioxidants, disinfectants, oestrogens and alkyl-phenols are among the trace organic chemicals (TOrCs) [1] that are widely employed in home and personal care products and pharmaceuticals [2-5]. The extensive inclusion of these chemicals in daily-life products [2] and their polar and non-volatile nature [6] has resulted in their widespread distribution in the aquatic environment across the world [7-9]. As a result, increasing concern has been raised about their potential long-term effects on human health [2, 10, 11] and wildlife [4, 12]. Monitoring the concentrations of these chemicals is the basic need for studying their fate and behaviour in aquatic environments, and providing data for further assessment of their potential transport through food chains and evaluating potential risks/toxicity on ecosystems and human health.

Many of the analytical methods for these chemicals in water samples have developed based on pre-treatment, normally solid-phase extraction (SPE) [1, 5, 13-15], followed by instrumental determination by gas chromatography-mass spectrometry (GC-MS) [14, 16, 17] or liquid chromatography-tandem mass spectrometry (LC-MS/MS) [1, 18-20]. With the rapid development of the technology, LC-MS/MS techniques have become preferred analytical method for polar and/or non-volatile TOrCs analysis [13], which have advantages such as high selectivity, sensitivity and throughput, reduced analytical time and do not require derivatisation as some GC-MS procedures do [14]. This has led their widespread application for water/wastewater sample analysis [5, 18]. More recently, LC systems equipped with high resolution MS (LC-HRMS), such as time-of-flight (TOF) and Orbitrip MS, are increasingly popular as it is beneficial for both quantifying target analytes and identifying non-target analytes [13, 21, 22].

A considerable amount of research has been conducted to determine some of the trace organic chemicals, such as preservatives [2, 5, 15, 18, 23, 24], antioxidants [20, 24], disinfectants [1, 5, 15, 23], oestrogens [5, 15] or alkyl-phenols [5], in different matrices (water/wastewater [1, 5, 18, 20], sludge [15, 20], cosmetics [2], foodstuffs [24], biota [23] and etc.) using the LC-MS/MS, but few studies have provided simultaneous determination of all these TOrCs. Furthermore, few studies have comparative evaluation for conventional LC-MS/MS (triple-quadrupole MS) and LC-HRMS [25, 26], and a comparison on their quantification of these chemicals between triple quadruple MS with HRMS would be of great interest for laboratories having only one of them.

Therefore, the aims of this study were 1) to develop and optimise a rapid and sensitive method for the simultaneous extraction and determination of 20 trace organic chemicals (preservatives, antioxidants, disinfectants, oestrogens and alkyl-phenols) by SPE and LC-MS/MS, 2) to compare the performance of two different LC-MS systems: a triple-quadrupole MS (QqQ-MS) system and a hybrid quadrupole Orbitrap high resolution MS (Q- Orbitrap-HRMS) system for these chemicals, and 3) to apply this analytical method to determine the occurrence of these substances in river water and municipal wastewater collected from a city in central China.

2. Materials and Methods

2.1 Chemicals and materials

Twenty typical chemicals in 5 groups of TOrCs (preservative, antioxidant, disinfectant, oestrogens and alkyl-phenols) were selected in this study. High purity standards of these compounds, including 4-hydroxybenzoic acid (PHBA), methylparaben (MEP), ethylparaben (ETP), propylparaben (PRP), butylparaben (BUP), benzylparaben (BEP) and heptyl paraben (HEP), butylated hydroxyanisole

(BHA), butylated hydroxytoluene (BHT), ortho-phenylphenol (OPP), triclosan (TCS), triclocarban (TCC), bisphenol-A (BPA), diethylstilbestrol (DES), estrone (E1), β-estradiol (E2), estriol (E3), 17α-ethinylestradiol (EE2), 4-*tert*-octylphenol(4-*t*-OP) and nonylphenol (NP) were purchased from Sigma-Aldrich (UK). Detailed information of these TOrCs was given in Supporting Information (SI) **Table S1**. Internal standards (ISs) including ^{13}C MEP, ^{13}C BUP, ^{13}C PRP, ^{13}C BUP, BHA-d_3, ^{13}C OPP and BPA-d_{16} were purchased from Sigma-Aldrich (UK), other ISs including PHBA-d_4, BHT-d_{24}, TCS-d_3, E1-d_4, E2-d_5, E3-d_2. EE2-d_4, 4-n-OP-d_{17} and 4-n-NP-d_4 were purchased from QMX Laboratories (UK).

Reagents are at least analytical grade and ≥ 99 % purity, organic solvents are HPLC grade. formic acid (FA), acetic acid (HAc) and ammonia solution (NH_4OH, 5 M) were purchased from Sigma-Aldrich (UK). Hydrochloric acid (HCl, 35.5-37.5 %), ammonium formate (AF), ammonium acetate (NH_4Ac) methanol (MeOH), acetonitrile (ACN) and ethyl acetate (EA) were obtained from Fisher Scientific (UK). Water used in the experiments was supplied by a Milli-Q water (MQ water) purification system (> 18.2 MΩ cm^{-1}, Millipore, UK).

Stock solutions of each chemical standard (1000 mg L^{-1}) were prepared in methanol and stored in sealed amber bottles in the dark at -20 ℃ for later use. Working standard solutions (10 mg L^{-1}) were prepared weekly by diluting the stock solutions with methanol and stored at 4 ℃ before use. The calibration standards with increasing concentrations of analytes and 100 μg L^{-1} ISs were prepared in MeOH/MQ water (1:1) with/without additives.

2.2 Water samples

Freshwater samples from the River Conder (Lancaster, UK) and wastewater samples (both influent and effluent) from a UK WWTP (traditional activated sludge treatment process and the service

population of ca. 100 000) were collected in clean amber bottles for the optimisation experiments. River water and wastewater samples from China were collected for environmental analysis. The bottles were fully immersed and soaked in Decon 90 solution (4 %) overnight and then rinsed thoroughly with tap water and MQ water, followed by baking at 450 ℃ for 4 hours (h) before use. The bottles were rinsed by water samples for 3 times before taking final samples. The water samples were transported to the laboratory after collection and stored in the dark room at 4 ℃ and extracted in 24 h.

2.3 Solid-phase extraction and reconstruction

Solid-phase extraction (SPE) was used for extracting the trace organic chemicals from the water samples. Reversed-phase SPE cartridges are commonly-used for extraction of TOrCs waste waters [15, 18]. Three types of widely-used reversed-phase SPE cartridges were used in this study: Oasis-HLB SPE cartridges, Supel-Select HLB tubes and Strata-X tubes were purchased from Waters (UK), Sigma-Aldrich (UK) and Phenomenex (UK), respectively. Detailed information of SPE cartridges used in this study was given in **Table S2**.

To optimise the SPE method, several procedures were carried out including 1) adjustment of pH (2.5 or 7) for water samples before filtration, 2) selection of SPE cartridges (Oasis-HLB, Supel-Select HLB and Strata-X) and 3) selection of elution solvents (MeOH, ACN, EA and their mixture). 100 ng L^{-1} of individual TOrC were spiked into the river water samples for SPE optimisation, followed by determination using System A, the LC-QqQ-MS.

After pH adjustment, the water samples were filtered (Whatman GF/F filter, 0.7 μm) to remove suspended particles. A 500 mL sample was extracted separately by solid-phase extraction (SPE) using the three cartridges mentioned above. 100 ng of individual IS was added into filtered samples

126 before extraction. The SPE cartridges were preconditioned with 10 mL strong solvents (if applicable,
127 ACN, EA or mixture), 10 mL MeOH followed by 10 mL MQ water, and the water samples were
128 then introduced into the cartridge at a flow rate of about 3 mL min^{-1}. The sample bottle was then
129 rinsed twice with two aliquots of 50 mL of 5 % (v/v) methanol in MQ water, which was also passed
130 through the cartridge. After loading, the cartridges were rinsed with 10 mL MQ water and vacuum
131 dried for 20 min. The TOrCs retained by the cartridges were finally eluted with 10 mL elution
132 solvent (MeOH, ACN, EA or their mixture). For the SPE optimisation on pH adjustment and SPE
133 cartridge selection, MeOH was used as the elution solvent, as it is the most commonly used SPE
134 solvent for the chemicals studied here.

135 Sample extracts were reduced to 1 mL under a gentle flow of N_2, followed by syringe filteration
136 (0.22 μm) and transfer to amber vials, stored at -20 ℃ before instrumental analysis. Just prior to the
137 instrumental analysis, 300 μL aliquot of each sample extract (200 μL for influent) were dried under
138 a gentle N_2 flow and reconstituted in 100 μL of water and methanol mixture (50:50, v/v) with the
139 same additives in the optimised mobile phase.

140 ## 2.4 Instrumental Analysis

141 ### 2.4.1 Instruments

142 For comparative purposes, the same samples were analysed by two different LC-MS systems, A:
143 LC-QqQ-MS and B: LC-Q-Orbitrap-HRMS. These two systems were selected in terms of
144 equipment and running cost and expected performance.

145 System A: The system consisted of an Agilent 1100 series HPLC system and a Quattro Micro
146 triple-quadrupole mass spectrometer (QqQ MS, Micromass, Manchester, UK). The HPLC system
147 was composed of a binary pump, a vacuum micro-degasser, an auto-sampler and a thermostatic

column compartment. The Quattro Micro triple-quadruple mass spectrometer was equipped with an electrospray ionisation (ESI) source. High-purity nitrogen was used as nebulising and desolvation gas supplied by a generator (Peak Scientific, UK), bottled argon (99.999%) was used as the collision gas. The instrument control and data acquisition were controlled by Masslynx 4.1 software.

System B: An ultrahigh performance liquid chromatography-high resolution mass spectrometer system (UHPLC-HRMS) with an Ultimate 3000 UHPLC (Dionex) coupled to a hybrid quadrupole-Orbitrap mass spectrometer (Q-Orbitrap MS, Q-Exactive, Thermo Fisher Scientific, Germany). The UHPLC system consisted of a quaternary pump, auto-sampler and a column compartment. The HR-MS is an Orbitrap based MS equipped with a heated electrospray ionization probe (HESI-II). High-purity nitrogen was used as sheath gas, auxiliary gas and collision gas. Xcalibur 3.0 software was used for instrument control and data acquisition.

2.4.2 LC-MS/MS and LC-HRMS determination

The selection of MS parameters was based on the most intense signal of fragmentation products for each chemical. The instrument-dependent MS parameters of System A, including capillary voltage, source temperature, desolvation temperature, cone gas flow and desolvation gas flow, and the chemical-dependent MS parameters, such as cone voltage (CV) and energy collision (CE), were also optimised by a continuous-flow mode of direct infusion, injecting the single chemical standard (1 mg L^{-1} in MeOH/MQ water, 1:1) by a syringe pump at the flow rate of 10 μL min^{-1}, into the stream of in MeOH/MQ water (1:1) at the flow rate of 0.2 mL min^{-1} with various concentrations of different mobile phase additives. Similarly, instrument-dependent MS parameters of System B, including spray voltage, capillary temperature, sheath gas flow, auxiliary gas flow, sweep gas flow,

spray current, S-Lens RF level, auxiliary gas heater temperature and the normalised collision energy (NCE) for individual TOrC were also optimised by the same procedure above.

To improve separation by the LC and the MS performance, especially the ESI sensitivity performance, several mobile phases (MeOH, ACN and MQ water) and their additives were considered, including FA (0-0.2 %), HAc (0-1 %), AF (0-10 mM) and NH_4Ac (0-10 mM) and NH_4OH (0-10 mM). The influence of these additives on instrument sensitivity was studied by the same procedure of direct infusion as described above.

After initial analyses, the following composition of mobile phase and additives was chosen for LC separation and maximisation of the MS responses for both systems: mobile phase A: 95 % MQ water, 2.5 % ACN and 2.5% MeOH with 5 mM NH_4OH; mobile phase B: 95 % ACN, 2.5 % MeOH and 2.5 % MQ water with 5 mM NH_4OH. LC separation was carried out on an Xbridge BEH C18 column (100 mm × 2.1mm, 2.5 μm, Waters, UK) with a pre-column. The optimised gradient procedure was: 0 - 1 min 15 % B, then increased to 80 % B within 9 min, followed by reaching to 100 % B in 5 min, held for 4.5 min, then back to the initial condition (15 % B) in 0.5 min, finally, a post-run of 10 min to re-equilibrate of the column before the next injection. The total running time for each sample is 30 min. The injection volume was 10 μL and the column compartment temperature was kept at 25 ℃

System A was optimally operated in negative ion mode with a capillary voltage of 3 kV, a source temperature of 120 ℃ and a desolvation temperature of 300 ℃, no cone gas flow and a desolvation gas flow of 600 L h^{-1}.

The analysis using System B was optimised and performed in the negative ion mode with a spray

voltage of 2.5 kV, a capillary temperature of 320 ℃, a sheath gas flow of 35 arbitrary units (arb), an auxiliary gas flow of 8 arb, a sweep gas flow of 5 arb, a spray current of 0 μA, S-Lens RF level of 45 arb, and an auxiliary gas heater temperature of 300 ℃. Fragmentation mass spectra were recorded at a mass resolution of 35 000/ 70 000 full width at half-maximum (FWHM) with a quadrupole isolation window of 1.0 Da for precursor ions, the AGC (automatic gain control) target was 5×10^4, and the maximum injection time (IT) was set to 40 milliseconds (ms).

2.5. Recoveries and matrix effect

Based on the published literature[27-29], distinction between SPE recoveries for the sample pre-treatment, matrix effects during the LC-MS/MS analysis and overall method recoveries for the whole method was conducted by spiking samples before/after optimised SPE procedures with the same amount of analytes. Samples (river water, wastewater influent and effluent) were spiked with the selected organic chemicals and ISs before SPE and after SPE. Additionally, samples without spiking were also measured to allow for subtracting the signal from the spiking samples. The TOrCs response factors (RFs, after non-spiked sample signal subtraction) of all the spiked samples were then compared with RFs of the standards. Thus, three types of RFs were acquired: one from the pure standard (*R1*), another from the pre-spiked samples (*R2*), and the last one from the post-spiked samples (*R3*). The matrix effect (*ME*, %), SPE recovery (RE_{SPE}, %) and the overall method recoveries ($RE_{overall}$, %) can be expressed by Equation (1), (2) and (3), respectively:

$$\text{Matrix effect:}\quad ME(\%) = \frac{R3}{R1} \times 100 \tag{1}$$

$$\text{SPE recovery:}\quad RE_{\text{SPE}}(\%) = \frac{R3}{R2} \times 100 \tag{2}$$

$$\text{Overall method recovery:}\quad RE_{\text{OVERALL}}(\%) = \frac{R2}{R1} \times 100 \tag{3}$$

ME (%) > 100 % indicates a signal enhancement, whereas the value < 100% indicates signal

suppression. It should be pointed out that the RE_{SPE} represents a true recovery for the SPE extraction procedures only, which is not affected by matrix [28].

2.6. Quantification and method validation

For System A, the target TOrCs were quantified by simultaneously recording at least two highest characteristic transitions from the $[M-H]^-$ precursor ion to the selected product ions in the multiple reaction monitoring (MRM) mode. For each chemical, the most intense transition was selected for quantification and the second one used for confirmation (**Tables 1** for the target TOrCs and **Table S3** for ISs, **Figure S1** for the chromatograms). The optimisation of precursor ion /product ion transitions was based on the QuanOptimize function in Masslynx 4.1. For System B, the quantification of the target compounds were carried out at both target-selected ion monitoring (t-SIM) and target-MS2 (t-MS2) scanning modes (TCS and BHT for t-SIM mode only, due to the instability of product ions). The t-SIM mode of HRMS working at 70 000 FWHM resolution power is capable enough for determination of TOrCs in complex matrices using the accurate parent ions. For the t-MS2 mode of System B, the parent ions specified in the inclusion list are selected by the quadrupole, fragmented in the higher energy collision dissociation (HCD) cell with the specific fragmentation energy and then collected in the C-trap, with the daughter ions accurately recorded by the Orbitrap detector. To simplify the quantification procedures for HRMS, the highest response of the accurate ion for each chemical at the t-SIM scan mode was used for quantification (**Tables 1 and S3, Figure S2**).

Some instrumental and method validation parameters, such as linearity, range calibration curves, accuracy and precision and detection limits are also discussed for the quantification purposes.

235 **Table 1:** Optimised LC-MS/MS scan parameters for target TOrCs by both instruments.

TOrCs	Accurate MW[a]	LC-QqQ-MS				LC-Q-Orbitrap-HRMS		
		parent ion	daughter ions	CV	CE	parent ion	daughter ions	NCE
MEP	152.0473	151	92/136[b]	25	25/15	151.0388	92.0248/136.0145	50
ETP	166.0630	165	92/136	30	20/15	165.0546	92.0248/136.0145	55
PRP	180.0786	179	92/136	30	25/15	179.0704	92.0248/136.0145	55
BUP	194.0943	193	92/136	30	25/15	193.0862	92.0248/136.0145	55
BEP	228.0786	227	92/136	30	25/15	227.0708	92.0248/136.0145	50
HEP	236.1412	235	92/136	35	20/15	235.1335	92.0248/136.0145	50
PHBA	138.0317	137	93	20	15	137.0231	93.0326	20
BHA	180.1150	179	164/149	20	15/25	179.1067	164.0824/149.0588	55
BHT	220.1827	219	204/163	30	25/30	219.1748	-[c]	-
OPP	170.0732	169	141/115	35	25/30	169.0648	141.0690/115.0533	90
TCS	287.9512	287/289	35	15	5	286.9443/288.9412	-	-
TCC	313.9780	313/315	160/162	20	15/15	312.9713/314.9682	159.9707/161.9676	10
BPA	228.1150	227	212/133	35	15/25	227.1072	212.0822/133.0638	60
DES	268.1463	267	237/251	40	30/25	267.1388	237.0905/215.1063	60
E1	270.1620	269	145/143	50	35/55	269.1545	145.0639/159.0806	70
E2	272.1776	271	183/145	55	40/40	271.1702	145.0639/183.0797	85
E3	288.1725	287	145/183	55	40/45	287.1649	145.0638/171.0795	90
EE2	296.1776	295	145/159	55	40/45	295.1700	145.0639/159.0796	75
4-t-OP	206.1671	205	134/133	35	25/20	205.1590	133.0638	60
NP	220.1827	219	133/147	35	35/30	219.1748	133.0638	60

236 a MW: molecular weight;

237 b A/B: quantification ion / confirmation ion;

238 c -: not applicable.

239 ### 2.6.1 Linearity, range and calibration curves

240 Linearity and range of the analytical procedure were tested by dilution of stock solutions.
241 Concentration levels from 0 to 1 mg L^{-1} were used for each TOrC. A multi-component internal
242 standard calibration curve (from 0.1, 0.25, 0.5, 1, 2.5, 5, 10, 25, 50, 100, 250, 500 to 1000 μg L^{-1} for
243 each TOrC, and 100 μg L^{-1} for each internal standard) was established for quantification.

244 ### 2.6.2 Accuracy and precision

245 Method accuracy was evaluated with the percentage of deviation of results for samples with known
246 (added) amounts of analytes. Precision was estimated by the intra-day and inter-day reproducibility

using the relative standard deviation (RSD) of replicate measurements for both instrument and analytical method. 12 injections for spiked river water samples with 2 concentrations (10 and 200 μg L^{-1} of TOrCs were added before extraction, three replicates of each concentration) and standard samples with 2 concentrations (10 and 200 μg L^{-1}, three replicates of each concentration), were analysed over a short time interval on the same day under the same operating conditions to assess the intra-day precision. Similarly, 12 injections undertaken on three different days with the same concentrations were conducted to verify the inter-day precision.

2.6.3 Detection Limits (DL)

DLs for TOrCs were determined based on the signal-to-noise (S/N) methodology. DL is defined as the concentration that represents 3 times of the S/N. The IDLs (instrument DLs) of each TOrCs were calculated using standards with low concentrations, and MDLs (method DLs) for river water wastewater influent and effluent were estimated by IDLs, SPE absolute recoveries (RE_{SPE}, %) and the concentration factors (*CF*, 1000 for the influent and 1500 for effluent and river water) for TOrCs, using Equation (4) [19]:

$$MDL = \frac{IDL}{RE_{SPE} \times CF} \times 100 \quad (4)$$

2.7 Data analysis and statistics

All the laboratory experiments and field sample collection were carried out in triplicate unless stated specifically, and the results were expressed as the average ± standard deviation (SD). The statistical analysis was conducted by IBM *SPSS* Statistics software (Version 22), the significant differences were statistically tested by analysis of variance (ANOVA) at 5 % significant level.

3. Results and Discussion

3.1 Effect of mobile phases and additives

To optimise the LC separation and ESI ionisation, different organic mobile phases and the effect of mobile phase additives were studied. ACN was selected as the major organic mobile phase, because it could provide better separation and lower column pressure than MeOH. A small proportion (2.5 %) of MeOH and MQ water was added into organic mobile phase to enhance the solubility of additives.

Acid additives such as FA in the mobile phases are known to strongly suppress the signal in the ESI negative mode [18] when comparing with pure mobile phases, which was confirmed in this study (**Table S4**). The suppression for all the compounds increased with higher concentrations of acids which is due to the presence of these organic acids converting the target chemicals into their neutral form, which decreasing their MS response in negative ESI mode. The results using AF and NH_4Ac indicated that the presence of AF in the mobile phase could also suppress the signals for all the compounds in negative ESI mode, but showed less suppression than FA. The addition of NH_4Ac at about 5 mM concentration caused enhancement of signals for antioxidants, disinfectants, oestrogens and alkyl-phenols, but resulted in a slight suppression of signals for parabens.

Basic additives such as ammonia and amines can also be used for LC-ESI-MS analysis. In this study, only ammonia was tested with amines not considered because of their strong retention in the LC-MS system, which may lead to signal suppression. The results showed strong enhancement of the ESI negative response for all TOrCs when adding NH_4OH at 5-10 mM into the mobile phase. The majority of the tests were conducted with System A but also confirmed using System B.

Based on results of the effect of mobile phase additives on signal response, a 5 mM ammonia solution was added into both organic and aqueous mobile phases for the optimised instrumental analysis procedures. The same concentration of ammonia solution was also added into the final samples prior to the LC-MS analysis.

3.2 Optimisation of SPE conditions

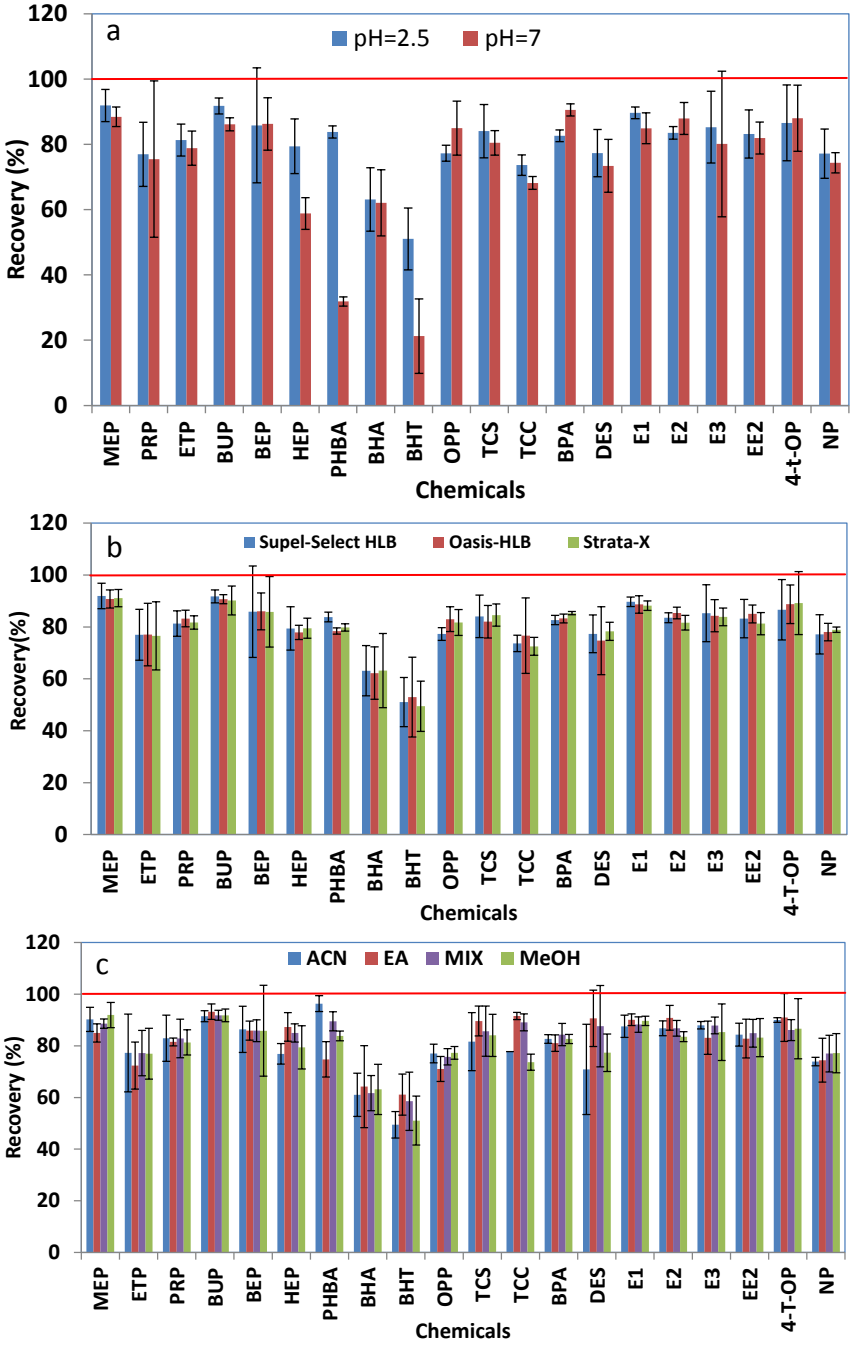
The SPE conditions were optimised using 500 mL river water samples spiked with 100 ng L^{-1} (50 ng) of individual TOrCs, followed by further pre-treatment and processing. The effects of water sample pH and elution solvents and different SPE cartridges were tested to achieve the best recoveries for target TOrCs.

3.2.1 pH effect

Water sample pH was normally adjusted for better retention on reversed-phase SPE cartridges. It has been suggested that the pH for the samples should be adjusted to 2 pH units below the most acidic analytes' pK_a [30]. Thus, river water samples were adjusted to pH 2.5 (the smallest pK_a value for all target compounds is about 4.38 for PHBA) 7, followed by extraction using Supel-Select HLB tubes to test the effect of sample pH on recoveries. The same water samples were also adjusted to pH 7 (natural condition) for comparison of pH effects. The results (**Figure 1a**) show that recoveries at pH 2.5 (51.0 ± 9.5 to 91.9 ± 2.5 %) were better than at pH 7 (21.3 ± 11.4 to 90.6 ± 1.8 %) for most TOrCs, especially for HEP, PHBA and BHT. There were no significant differences (ANOVA, $p > 0.05$) in recoveries for oestrogens and alkyl-phenols between pH 2.5 and 7, which was similar to results from Liu *et al* and Gonzalez-Marino *et al* [18, 31]. Because of the improved performance under pH 2.5, all water samples were acidified to pH 2.5 for further SPE optimisation.

3.2.2 SPE cartridge selection

Three types of reversed-phase SPE cartridges/tubes, including Oasis-HLB, Supel-Select HLB and Strata-X were tested for chemical recoveries (information of three kinds of SPE cartridges were given in **Table S2**). The results in **Figure 1b** indicated that, for the majority of TOrCs, no significant differences (ANOVA, $p > 0.05$) of SPE recoveries were found among three kinds of SPE cartridges. All these three SPE cartridges could provide good and stable recoveries (> 75 %) for the majority of TOrCs, with the exception of BHA, BHT, TCC and DES. Considering other factors such as the availability and price (**Table S2**), Supel-Select HLB tubes were selected for further test with the elution on solvents.



318

319 **Figure 1**: Effects of pH (a), SPE cartridges (b) and eluting solvents (c) on the SPE recoveries (n=3).

320 ### 3.2.3 Eluting solvent effect

321 Three organic solvents (MeOH, ACN and EA) were tested to assess which achieved the best SPE

322 recoveries, especially for PHBA, BHA, BHT, TCC and DES. The results (**Figure 1c**) show that

323 each individual solvent still has some drawbacks for eluting all the target chemicals: ACN could

achieve better recoveries for PHBA (96.3 ± 3.1 %) but not for BHT, TCC and DES, EA could elute more BHT, TCC and DES but less PHBA, and MeOH has medium eluting for these chemicals. Thus, the mixture of ACN and EA (50 % : 50 %, v/v) was selected for further test and good recoveries (> 75 %) were obtained for all TOrCs except BHA and BHT (61.7 ± 6.8 % and 58.8 ± 11.3 %), which ranged from 75.7 ± 3.2 % to 91.8 ± 1.9 %.

3.2.4 SPE recoveries for optimised procedures

Based on the tests above, the extraction procedures were fully optimised and then applied to SPE recoveries, overall recoveries and matrix effect test and the field application for the environmental samples. The SPE recoveries were evaluated using the optimised SPE procedures by spiking 100 ng L^{-1} of TOrCs in the influent, effluent and river water, and followed by analysis using both instruments. The results are shown in **Figure 2**, providing good SPE recoveries for the majority of the TOrCs when both systems were applied for the analysis.

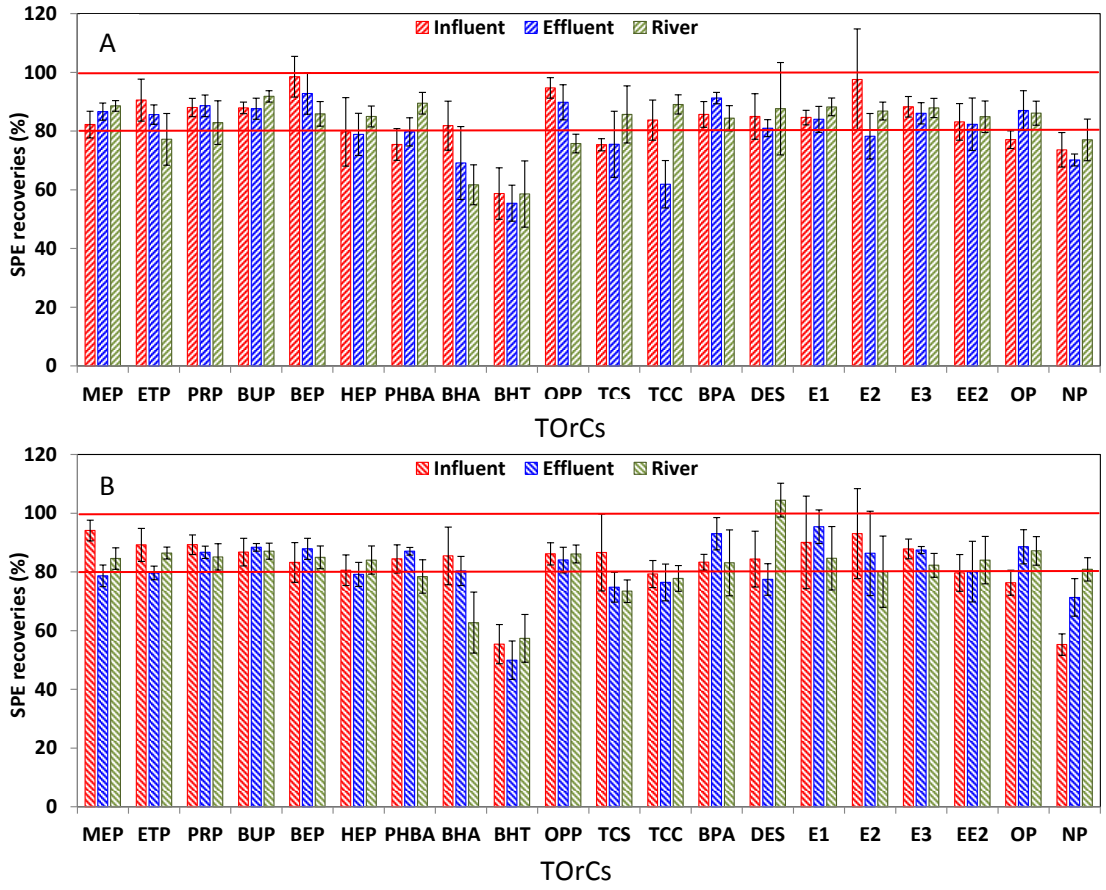


Figure 2: SPE recoveries of selected organic chemicals in influent, effluent and river water samples (n = 3) with both instruments (A: LC-QqQ-MS system and B: LC-Q-Orbitrap-HRMS system), Error bar: 1SD.

3.3 LC-MS/MS and LC-HRMS quantification, performance and method validation

The MS parameters for both LC-MS systems were optimised based on the most intense signal of fragmentation products for each TOrC. The results from the optimization of the MS parameters and quantification for both LC-MS systems are contained in parts of ***2.4.2 LC-MS/MS and LC-HRMS determination*** and **Table 1**. Following this the instruments were operated for sample analysis. Due to the scan range limitation (50 Da minimum) of the HRMS, no daughter ion of TCS could be detected. As the resolution of 70 000 FWHM is capable enough for determination of the selected TOrCs, only results from t-SIM mode of LC-HRMS were used for the comparative evaluation with

LC-QqQ-MS.

The equations, linear ranges and linearity correlation coefficients (R^2) of the calibration curves, the IDLs and MDLs for both systems are contained in **Table S5** and **Table 2**. The linear ranges of LC-QqQ-MS and LC-Q-Orbitrap-HRMS systems are 2.5-1000 μg L^{-1} and 0.25-500 μg L^{-1} for the majority of TOrCs, respectively, showing good linear ranges for both instruments. Both instruments could achieve excellent linearity (R^2 > 0.99 for all TOrCs, and R^2 > 0.999 for some of them). Precision of both the instruments and method were evaluated intra-day and inter-day for the two LC-MS systems by injection of 3 replicates of standard solutions and spiked river water samples at both 10 and 200 μg L^{-1}. Good method precision for both systems was obtained showing the intra-day and inter-day RSDs ranged from 0.5-4.8 % and 2.1-8.1 % for LC-QqQ-MS and 0.5-8.4 % and 0.8-9.5 % for LC-Q-Orbitrap-HRMS taking the results of 200 μg L^{-1} as an example. Better linearity (closer to 1 of R^2) and smaller RSDs for the majority of TOrCs were observed for LC-QqQ-MS comparing with LC-Q-Orbitrap-HRMS, which is similar with a previous study on hexabromocyclohexane (HBCD) using QqQ-MS and Orbitrap-HRMS[26]. These results demonstrated that the LC-QqQ-MS system is more stable for batch analysis of environmental samples.

The instrument detection limits (IDLs) and method detection limits (MDLs) in wastewater and river water for individual TOrCs are listed in **Table 2**. Remarkable differences were observed between the two systems with the LC-Q-Orbitrap-HRMS system being more sensitive than the LC-QqQ-MS system which provided 2-33 times lower IDLs for individual TOrCs. This may have resulted from the loss of response when daughter ions were produced in collision cell. The MDLs for the LC-QqQ-MS system were calculated based on the IDLs, and ranged from 0.48-23.3 ng L^{-1},

0.33-16.4 ng L^{-1} and 0.32-15.6 ng L^{-1} for the influent, effluent and river water, respectively, showing comparable data with recent publications [1, 5, 20]. These values are low enough for analysis of the environmental samples. The The MDLs provided by the LC-Q-Orbitrap-HRMS system are lower than these publications, which are 0.06-1.41 ng L^{-1}, 0.04-1.04 ng L^{-1} and 0.04-0.91 ng L^{-1} for the influent, effluent and river water, respectively.

Table 2: Performance (R^2, IDLs and MDLs) of both instruments for standard & environmental samples (A: LC-QqQ-MS system and B: LC-Q-Orbitrap-HRMS system).

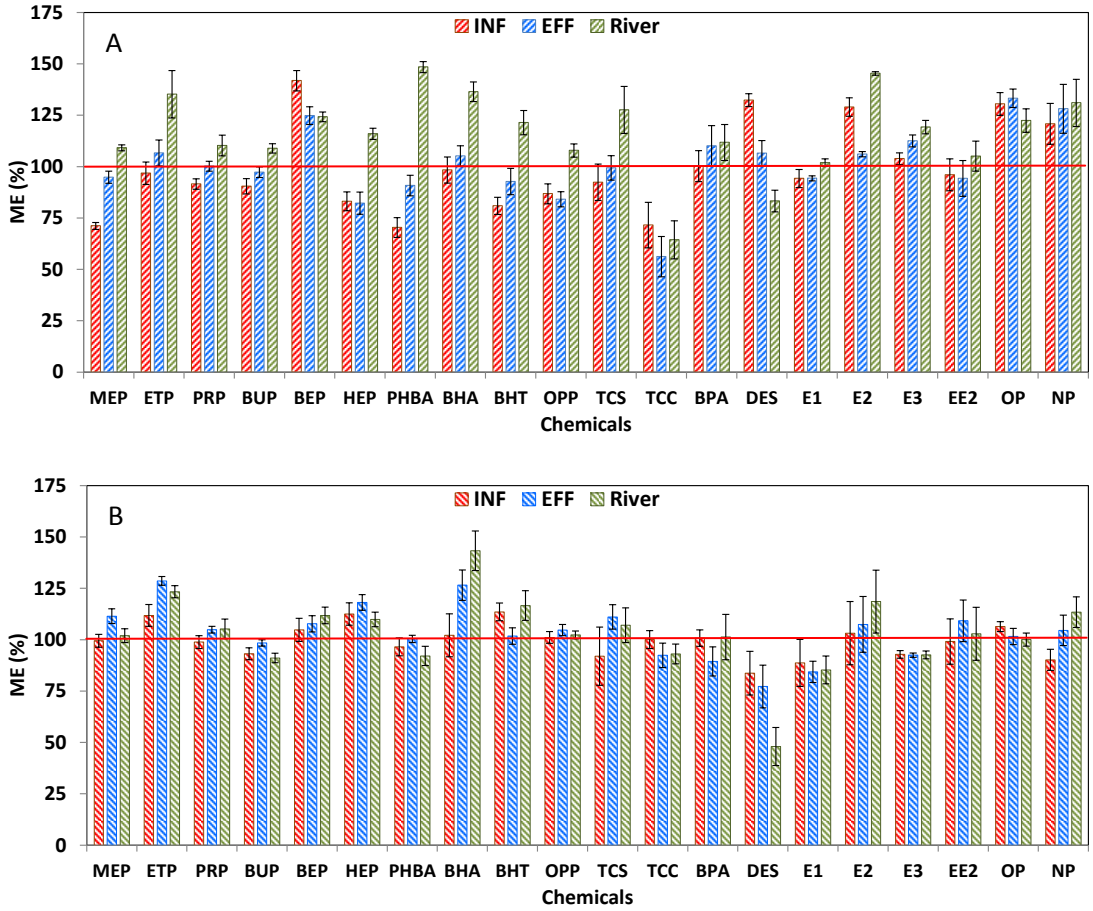
TOrCs	R^2		IDL, ng mL^{-1}		MDL, ng L^{-1}					
					Influent water		Effluent water		River water	
	A	B	A	B	A	B	A	B	A	B
MEP	0.9992	0.9990	0.88	0.38	1.07	0.40	0.68	0.32	0.66	0.30
ETP	0.9996	0.9973	2.47	0.37	2.73	0.41	1.93	0.31	2.14	0.29
PRP	0.9998	0.9981	1.22	0.15	1.38	0.17	0.92	0.12	0.98	0.12
BUP	0.9994	0.9991	1.47	0.13	1.67	0.15	1.12	0.10	1.07	0.10
BEP	0.9998	0.9995	2.24	0.11	2.27	0.13	1.61	0.08	1.74	0.09
HEP	0.9986	0.9951	3.00	0.09	3.76	0.11	2.54	0.08	2.35	0.07
PHBA	0.9997	0.9996	3.95	0.62	5.24	0.73	3.31	0.47	2.95	0.53
BHA	0.9987	0.9982	3.42	0.13	4.17	0.15	3.29	0.11	3.69	0.14
BHT	0.9964	0.9979	13.7	0.78	23.3	1.41	16.4	1.04	15.6	0.91
OPP	0.9992	0.9992	0.63	0.05	0.67	0.06	0.47	0.04	0.56	0.04
TCS	0.9904	0.9986	2.16	0.07	2.87	0.08	1.91	0.06	1.68	0.06
TCC	0.9950	0.9958	0.44	0.05	0.53	0.06	0.47	0.04	0.33	0.04
BPA	0.9973	0.9959	1.10	0.19	1.28	0.23	0.80	0.14	0.87	0.15
DES	0.9994	0.9985	1.78	0.16	2.10	0.19	1.47	0.14	1.36	0.10
E1	0.9994	0.9995	2.80	0.14	3.31	0.16	2.22	0.10	2.12	0.11
E2	0.9984	0.9983	0.89	0.33	0.91	0.35	0.76	0.25	0.68	0.27
E3	0.9997	0.9987	0.42	0.26	0.48	0.30	0.33	0.20	0.32	0.21
EE2	0.9986	0.9949	0.89	0.13	1.08	0.16	0.72	0.11	0.70	0.10
4-t-OP	0.9994	0.9993	1.80	0.47	2.34	0.62	1.38	0.35	1.39	0.36
NP	0.9989	0.9988	0.75	0.36	1.02	0.65	0.71	0.34	0.65	0.30

3.4 Matrix effect and overall recoveries

Matrix effects are one of the main drawbacks of LC-MS with ESI mode, which can lead to signal suppression or enhancement due to the presence of matrix in the sample [27, 28]. This phenomenon is difficult to eliminate through sample pre-treatment procedures, but can be compensated/corrected

by the use of stable isotope-labelled internal standards (SIL-ISs) [28]. Matrix effects were studied and evaluated by processing samples of river water, wastewater effluent and influent with the optimised SPE method and pre-/post-spiking with 100 ng of the individual analytes. The matrix effects (ME, %) for the influent, effluent and river water were calculated using Equation (1) and presented in **Figure 3** for both systems.

No remarkable signal suppression or enhancement was observed for the majority of TOrCs when LC-Q-Orbitrap-HRMS was employed to analyse the samples. Similar results were observed for effluent samples when the LC-QqQ-MS system was used, but significant ME of influent and river water samples were found for the majority of TOrCs, especially for those chemicals that did not have the SIL-ISs such as BEP, HEP, TCC and DES. Similar phenomena of SIL-ISs influence on MEs were also observed in previous studies on preservatives, antioxidants[18] and oestrogens [32], confirming the advantage of SIL-ISs on the compensation for ME. Relatively large differences of ME were observed between the two LC-MS systems in this study, which is consistent with previous studies[18], showing that the matrix effects may vary greatly between different LC-MS systems due to the different design of ESI sources among manufactures[18, 28]. These results indicated that ME should be considered and re-evaluated when translating a LC-MS method among different instruments.



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399 **Figure 3:** Matrix effects of TOrCs in influent, effluent and river water samples (n = 3) with both instrumental

400 setups (A: LC-QqQ-MS system and B: LC-Q-Orbitrap-MS system), Error bar: 1SD.

401 Optimised SPE procedures were conducted to measure the overall recoveries analysed by both

402 instruments for river water and wastewater spiked with different concentrations of selected TOrCs

403 (10 and 100 ng L^{-1} for river water, 20 and 200 ng L^{-1} for effluent and 50 and 400 ng L^{-1} for influent).

404 **Table 3** showed the average of overall recoveries for spiked wastewater and river water samples

405 analysed both instruments. All recoveries were acceptable for both freshwater and wastewater

406 samples. Due to the smaller matrix effect for the LC-Q-Orbitrap-HRMS system, better overall

407 recoveries were observed for this system, and the overall recoveries fell in to the range of 80-120 %

408 for the majority of TOrCs.

409

410 **Table 3:** Overall recoveries (average ± SD, %)) for both instruments (n=3, A: LC-QqQ-MS system and B: LC-Q-Orbitrap-HRMS system).

TOrC	Influent				Effluent				River water			
	50 ng L^{-1}		400 ng L^{-1}		20 ng L^{-1}		200 ng L^{-1}		10 ng L^{-1}		100 ng L^{-1}	
	A	B	A	B	A	B	A	B	A	B	A	B
MEP	71.8 ± 3.5	91.8 ± 7.3	72.1 ± 3.1	93.6 ± 3.2	76.6 ± 5.2	110 ± 6.2	96.1 ± 3.4	87.7 ± 2.9	69.7 ± 7.2	83.9 ± 6.1	98.0 ± 2.2	86.2 ± 3.2
ETP	83.9 ± 3.9	119 ± 11	97.4 ± 1.8	110 ± 2.9	92.1 ± 5.7	85.5 ± 1.9	107 ± 4.7	113 ± 2.7	96.4 ± 9.2	97.8 ± 2.1	105 ± 1.2	118 ± 1.6
PRP	101 ± 6.6	94.5 ± 4.3	103 ± 2.8	96.9 ± 4.5	95.9 ± 7.6	93.5 ± 4.2	113 ± 2.3	99.7 ± 4.8	94.4 ± 4.9	94.8 ± 3.3	103 ± 4.0	98.3 ± 4.1
BUP	82.8 ± 1.3	96.5 ± 3.2	87.8 ± 2.6	95.3 ± 6.2	82.5 ± 0.9	91.7 ± 4.1	94.4 ± 2.1	103 ± 4.2	81.9 ± 2.6	85.6 ± 3.8	97.1 ± 2.4	93.6 ± 4.9
BEP	113 ± 17	111 ± 0.8	148 ± 3.2	101 ± 3.9	113 ± 6.8	98.8 ± 1.1	130 ± 3.7	109 ± 2.4	95.5 ± 7.6	97.6 ± 2.2	112 ± 3.0	109 ± 2.6
HEP	59.4 ± 2.1	114 ± 6.0	71.6 ± 6.3	117 ± 2.5	60.6 ± 3.2	104 ± 7.7	70.8 ± 10	121 ± 3.0	72.7 ± 4.3	96.2 ± 9.1	84.9 ± 4.6	119 ± 4.0
PHBA	64.9 ± 7.7	127 ± 3.6	59.4 ± 3.9	94.2 ± 1.8	69.4 ± 6.6	118 ± 3.1	76.7 ± 4.4	101 ± 0.9	87.9 ± 7.4	118 ± 3.9	112 ± 5.0	83.4 ± 2.3
BHA	83.4 ± 7.1	94.3 ± 9.6	93.3 ± 8.1	103 ± 3.8	88.3 ± 7.2	100 ± 11	99.8 ± 5.5	110 ± 2.0	80.3 ± 9.3	103 ± 9.1	105 ± 4.1	106 ± 5.3
BHT	77.9 ± 9.8	80.5 ± 4.8	90.2 ± 4.3	86.8 ± 7.6	79.0 ± 9.2	86.9 ± 3.5	103 ± 4.7	92.8 ± 7.9	71.6 ± 4.3	74.0 ± 2.4	79.2 ± 7.8	91.7 ± 6.2
OPP	88.1 ± 2.9	101 ± 9.0	101 ± 7.4	110 ± 1.1	86.2 ± 2.9	87.9 ± 9.8	97.6 ± 6.1	111 ± 1.8	86.2 ± 4.5	88.8 ± 9.2	94.8 ± 6.3	111 ± 1.4
TCS	110 ± 9.0	105 ± 3.1	85.0 ± 7.7	106 ± 4.0	109 ± 8.2	108 ± 8.9	91.5 ± 1.4	110 ± 4.1	105 ± 8.1	91.4 ± 3.2	101 ± 3.5	104 ± 0.5
TCC	105 ± 19	107 ± 3.8	103 ± 5.6	114 ± 3.8	49.6 ± 13	91.7 ± 7.6	80.9 ± 5.6	101 ± 3.9	65.7 ± 16	83.4 ± 7.1	82.5 ± 2.6	104 ± 3.1
BPA	120 ± 12	118 ± 7.6	121 ± 3.0	109 ± 5.4	108 ± 15	96.4 ± 9.3	133 ± 3.2	108 ± 5.2	88.4 ± 12	88.1 ± 8.3	114 ± 4.2	109 ± 6.9
DES	125 ± 7.0	118 ± 9.4	118 ± 2.9	100 ± 13	71.5 ± 14	84.6 ± 14	94.7 ± 4.8	84.8 ± 9.0	46.1 ± 8.7	56.7 ± 12	64.8 ± 14	71.1 ± 11
E1	111 ± 4.4	91.7 ± 5.0	100 ± 3.1	107 ± 8.3	96.8 ± 8.7	86.3 ± 6.8	100 ± 4.4	108 ± 4.5	94.9 ± 5.3	87.2 ± 8.5	95.5 ± 4.3	96.5 ± 8.0
E2	97.0 ± 9.5	98.6 ± 17	102 ± 6.4	99.4 ± 15	101 ± 8.5	90.5 ± 17	83.9 ± 19	96.0 ± 16	98.6 ± 9.6	91.2 ± 13	99.8 ± 5.2	98.3 ± 12
E3	106 ± 6.1	87.7 ± 3.9	101 ± 2.1	95.9 ± 3.6	97.5 ± 6.9	81.8 ± 4.3	110 ± 2.0	95.1 ± 2.3	99.6 ± 6.1	79.9 ± 5.6	102 ± 1.4	89.6 ± 4.3
EE2	86.2 ± 7.4	90.0 ± 5.7	99.4 ± 8.1	88.7 ± 5.7	85.7 ± 8.3	79.3 ± 8.1	97.6 ± 4.4	98.2 ± 11	84.9 ± 7.9	80.8 ± 4.4	92.4 ± 5.0	97.1 ± 5.6
4-t-OP	142 ± 9.7	108 ± 6.0	121 ± 6.0	97.2 ± 5.4	136 ± 7.8	103 ± 2.2	124 ± 3.3	108 ± 5.4	125 ± 9.0	92.3 ± 2.5	130 ± 3.1	105 ± 5.2
NP	115 ±5.0	67.8 ± 0.9	125 ± 0.9	70.4 ± 2.9	108 ± 9.0	88.8 ± 3.7	133 ± 2.7	100 ± 3.4	98.9 ± 7.0	105 ± 8.3	112 ± 4.4	123 ± 0.9

411

3.5 Environmental application

This new multi-residual method for analysing trace organic chemicals was applied to determine their concentrations in surface waters and wastewaters. Grab water samples were collected from a river and a WWTP (influent and effluent) in a central city of China. Both instruments were used to analyse the river water and the wastewater water samples after the SPE, with similar results (**Table 4**) being found by these two instruments. Fewer chemicals were detected by LC-QqQ-MS due to the higher MDLs. Very low concentrations, or below the MDLs could be observed in the river water samples, but higher concentrations were present in the wastewater, especially in the influent. These results are shown in **Table 4** and indicate that the traditional WWTP did not efficiently remove all the TOrCs, resulting in their discharge into the receiving water. This demonstrated that the analytical method is capable of determining the TOrCs in the environmental samples.

Table 4: Concentrations (average ± SD, ng L^{-1}) of TOrCs in river water and wastewater samples (n=2) from a city of Central China (A: LC-QqQ-MS system and B: LC-Q-Orbitrap-HRMS system).

TO	Influent		Effluent		River water	
	A	B	A	B	A	BB
MEP	939 ±118	817 ±185	13.9 ±4.06	16.0 ±2.26	7.67 ±1.52	12.2 ±1.85
ETP	51.3 ±6.68	55.1 ±1.59	2.78 ±1.44	2.06 ±0.58	< MDL	1.82 ±0.20
PRP	19.1 ±0.19	26.5 ±2.33	1.01 ±0.15	1.44 ±0.29	< MDL	0.96 ±0.08
BUP	< MDL	1.51 ±0.11	< MDL	1.08 ±0.04	< MDL	0.98 ±0.05
BEP	< MDL	1.13 ±0.14	< MDL	0.74 ±0.10	< MDL	0.97 ±0.03
HEP	< MDL	0.87 ±0.02	< MDL	0.37 ±0.19	< MDL	0.65 ±0.06
PHBA	2324 ±200	2592 ±217	295 ±23.1	285 ±9.24	58.8 ±0.57	65.6 ±11.2
BHA	12.0 ±1.13	6.62 ±0.72	< MDL	1.10 ±0.09	< MDL	< MDL
BHT	70.6 ±5.69	59.7 ±8.58	51.0 ±5.93	56.3 ±6.59	< MDL	< MDL
OPP	26.0 ±7.38	26.2 ±1.51	4.35 ±1.23	4.17 ±0.11	2.16 ±0.22	2.22 ±0.23
TCS	22.5 ±1.97	19.5 ±0.52	17.9 ±0.35	17.6 ±0.44	9.47 ±1.48	5.71 ±0.02
TCC	8.23 ±0.72	7.63 ±0.49	1.25 ±0.26	0.90 ±0.15	0.40 ±0.16	0.41 ±0.06
BPA	52.3 ±1.51	47.6 ±2.56	19.5 ±2.05	16.3 ±3.72	1.88 ±0.13	2.12 ±0.61
DES	< MDL	1.01 ±0.01	< MDL	0.98 ±0.02	< MDL	0.93 ±0.01
E1	14.0 ±3.55	9.58 ±0.95	< MDL	0.56 ±0.12	< MDL	0.17 ±0.02
E2	9.44 ±0.76	8.77 ±1.22	2.34 ±0.20	2.42 ±0.26	< MDL	2.44 ±0.42

TO	Influent		Effluent		River water	
	A	B	A	B	A	BB
E3	33.5 ±3.85	30.8 ±0.66	3.12 ±0.06	2.65 ±1.35	2.46 ±1.23	0.64 ±0.01
EE2	5.13 ±0.31	3.04 ±0.12	2.34 ±0.07	2.66 ±0.06	1.02 ±0.25	2.12 ±0.03
4-T-OP	28.2 ±3.26	31.1 ±5.62	5.81 ±0.78	6.25 ±0.98	< MDL	< MDL
NP	593 ±22.9	504 ±27.7	174 ±16.7	191 ±11.3	< MDL	0.41 ±0.12

4. Conclusion

A sensitive and reliable analytical method has been developed for the simultaneous determination of preservatives, antioxidants, disinfectants, oestrogens and alkyl-phenols in surface water and wastewater samples by SPE followed by LC-MS analysis. SPE optimisation showed that extraction of 500 mL acidified (pH 2.5) water samples with Supel-Select HLB tubes (200 mg, 6 mL) followed by elution of 10 mL acetonitrile and ethyl acetate (50:50, v/v) mixture could provide good SPE recoveries (> 75 %) for most TOrCs selected for this study. The instrumental method was validated and evaluated for matrix effects using a QqQ-MS and a high resolution Q-Orbitrap-HRMS. Good performance with linearity and precision could be achieved by both systems, although the LC-QqQ-MS system performed better (closer to 1 of R^2) with a higher method precision (smaller RSDs), while the HRMS was more sensitive and less affected by matrix. Both instruments could achieve acceptable overall recoveries although higher recoveries were observed for the LC-Q-Orbitrap-HRMS system.

The results from a field sampling campaign collecting river water and WWTP influent and effluent from a city in central China confirmed the applicability of this proposed method to environmental samples.

Acknowledgement

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Supporting information for:

Simultaneous determination of 20 trace organic chemicals in waters by solid phase extraction (SPE) with triple-quadrupole MS (QqQ-MS) and hybrid quadrupole Orbitrap high resolution MS (Q-Orbitrap-HRMS)

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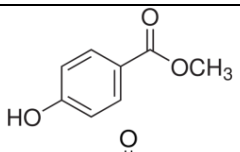
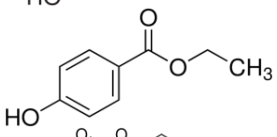
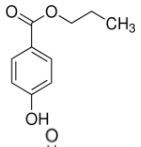
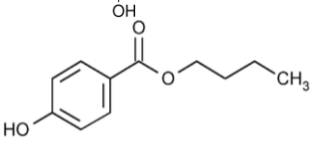
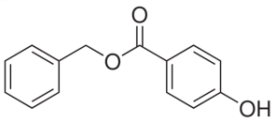
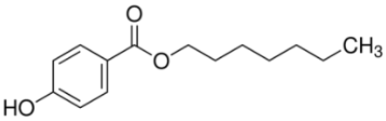
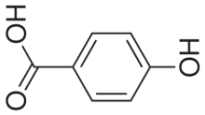
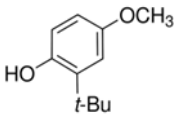
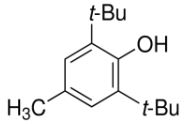
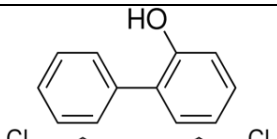
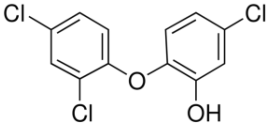
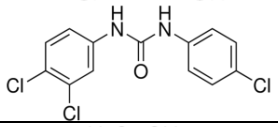
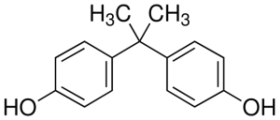
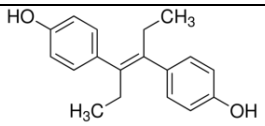
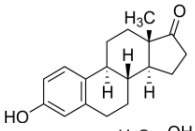
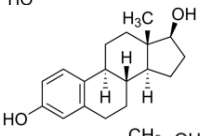
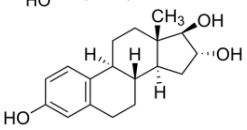
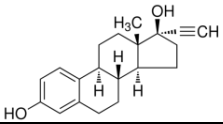
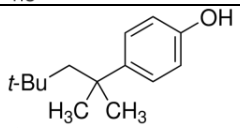
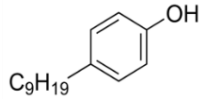
18 **Table S1:** Chosen trace organic chemicals and their properties[1].

19

Group	Chemical, ABBR[a] and purity	CAS No.	Molecular formula	MW[b,e]	Water solubility (mg L^{-1})[e]	pK_a[c,e]	LogK_{OW}[d,e]	Structure
Preservative	Methylparaben MEP ≥ 99.0%	99-76-3	$C_8H_8O_3$	152.15	2500	8.31	2	
	Ethylparaben ETP ≥ 99.0%	120-47-8	$C_9H_{10}O_3$	166.17	885	8.50	2.49	
	Propylparaben PRP ≥ 99.0%	94-13-3	$C_{10}H_{12}O_3$	180.2	500	8.23	2.98	
	Butylparaben BUP ≥ 99.0%	94-26-8	$C_{11}H_{14}O_3$	194.23	207	8.50	3.47	
	Benzylparaben BEP ≥ 99.0%	94-18-8	$C_{14}H_{12}O_3$	228.25	23.419	8.49	3.70	
	Heptyl paraben HEP ≥ 99.0%	1085-12-7	$C_{14}H_{20}O_3$	236.31	8.022	8.50	4.94	
	4-Hydroxybenzoic acid PHBA ≥ 99.0%	99-96-7	$C_7H_6O_3$	138.12	5000	4.38 9.67	1.39	
Antioxidant	Butylated hydroxyanisole BHA ≥ 98.0%	25013-16-5	$C_{11}H_{16}O_2$	180.24	212.8	10.55	3.5	
	Butylated hydroxytoluene BHT ≥ 99.0%	128-37-0	$C_{15}H_{24}O$	220.35	0.6	11.60	5.03	
Disinfectant	Ortho-phenylphenol OPP ≥ 99.0%	90-43-7	$C_{12}H_{10}O$	170.21	700	9.65	3.28	
	Triclosan TCS ≥ 97.0%	3380-34-5	$C_{12}H_7Cl_3O_2$	289.55	10	7.68	4.66	
	Triclocarban TCC ≥ 99.0%	101-20-2	$C_{13}H_9Cl_3N_2O$	315.59	0.65	11.42	4.90	
Estrogen	Bisphenol-A BPA ≥ 99.0%	80-05-7	$C_{15}H_{16}O_2$	228.29	120	9.65 10.45	3.64	

[1] This table is continued onto the next page.

Group	Chemical, ABBR[a] and purity	CAS No.	Molecular formula	MW[b,e]	Water solubility (mg L^{-1})[e]	pK_a[c,e]	LogK_{OW}[d,e]	Structure
	Diethylstilbestrol							
	DES	56-53-1	$C_{18}H_{20}O_2$	268.36	12	9.13 9.75	5.64	
	≥ 99.0%							
	Estrone							
	E1	53-16-7	$C_{18}H_{22}O_2$	270.37	30	10.33	3.43	
	≥ 99.0%							
	β-estradiol							
	E2	50-28-2	$C_{18}H_{24}O_2$	272.39	3.9	10.33	3.94	
	≥ 98.0%							
	Estriol							
	E3	50-27-1	$C_{18}H_{24}O_3$	288.39	440.8	10.33 13.62	2.81	
	≥ 97.0%							
	17α-Ethinylestradiol							
	EE2	57-63-6	$C_{20}H_{24}O_2$	296.41	11.3	10.33	4.12	
	≥ 98.0%							
	4-tert-octylphenol							
	4-t-OP	140-66-9	$C_{14}H_{22}O$	206.33	4.82	10.23	5.28	
Alkylphenol	≥ 97.0%							
	Nonylphenol							
	NP	84852-15-3	$C_{15}H_{24}O$	220.36	7.62	10.30	5.77	
	analytical standard							

[a] ABBR: abbreviation

[b] MW: molecular weight

[c] K_a: acid dissociation constant

[d] Kow: octanol–water partition coefficient

[e] the data were predicted by EPI Suite 4.1

27 **Table S2:** Properties of SPE cartridges/tubes.

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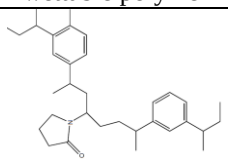
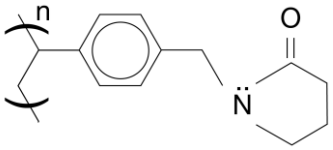
Name	Oasis-HLB	Supel-Select HLB	Strata-X
Manufacturer/Brand	Waters	Sigma-Aldrich	Phenomenex
Sorbent substrate	hydrophilic-lipophilic-balanced, water wettable polymer	Hydrophilic modified styrene based polymer	Functionalised polymeric sorbent
Structure		---	
Adsorption mode	Reversed-phase	Reversed-phase	Reversed-phase
Surface area (m^2 g^{-1})	727-889	160-420	800
Average pore diameter (Å)	73-89	80-200	85
Total pore volume (cm^3 g^{-1})	1.18-1.44	0.8-1.2	–
Average particle diameter (μm)	26-35	50-70	33
Mass spec compatibility	Yes	Yes	Yes
Water Wettable	Yes	Yes	Yes
pH range	1-14	1-14	1-14
Size (mL)	6	6	6
Sorbent weight (mg)	200	200	200
Price (£, 30/pack, without VAT)	117.0	91.5	135.0

29
30

Table S3: Optimised LC-MS/MS scan parameters for ISs by both instruments (A: LC-QqQ-MS system and B: LC-Q-Orbitrap-HRMS system).

Chemical	Accurate MW	A				B		
		parent ion	daughter ions	CV	CE	parent ion	daughter ions	NCE
MEP ^{13}C	158.0473	157	98/142[a]	25	25/15	157.0590	98.0448/142.0346	55
ETP ^{13}C	172.0630	171	98/142	30	20/15	171.0747	98.0448/142.0346	55
PRP ^{13}C	186.0786	185	98/142	30	20/15	185.0905	98.0448/142.0346	55
BUP ^{13}C	200.0943	199	98/142	30	20/15	199.1063	98.0448/142.0346	55
PHBA-d_4	142.0564	141	97	20	15	141.0483	97.0576	30
BHA-d_3	183.1335	182	164/149	20	15/25	182.1257	164.0824/149.0588	55
BHT-d_{24}	244.3309	242	223/179	45	35/35	242.3192	-[b]	-
OPP ^{13}C	176.0732	175	147/121	45	25/30	175.0850	147.0891/121.0734	90
TCS-d_3	290.9697	290/292	35	15	5	289.9631/291.9598	-	-
BPA-d_{16}	244.2138	241	142/223	45	25/25	241.1956	142.1203/223.1515	60
E1-d_4	274.1867	273	147/187	55	40/50	273.1797	147.0765/161.0920	75
E2-d_5	277.2085	276	187/147	50	40/40	276.2014	147.0764/187.1048	85
E3-d_2	290.1849	289	147/185	60	45/45	289.1776	147.0763/173.0921	90
EE2-d_4	300.2023	299	147/161	55	40/40	299.1952	147.0764/161.9210	75
4-n-OP-d_{17}	223.2720	222	108	35	25	222.2657	108.0529	65
4-n-NP-d_4	224.2074	223	110	35	20	223.1999	110.0655	65

a: quantification ion / confirmation ion;

b : not applicable.

Table S4: MS Response ratio of additives spiked mobile phase to pure mobile phase, expressed in average (n=3, standard deviation, SD).

Chemicals	Formic acid	Ammonium formate	Ammonium acetate	Ammonia
MEP	0.11 (0.01)	0.32 (0.02)	1.04 (0.18)	0.68 (0.02)
ETP	0.16 (0.01)	0.29 (0.01)	0.71 (0.06)	0.55 (0.01)
PRP	0.17 (0.10)	0.35 (0.01)	0.85 (0.08)	0.59 (0.02)
BUP	0.18 (0.01)	0.33 (0.02)	0.64 (0.06)	0.54 (0.03)
BEP	0.21 (0.00)	0.35 (0.01)	0.48 (0.04)	0.50 (0.01)
HEP	0.22 (0.01)	0.34 (0.01)	0.55 (0.02)	0.55 (0.01)
PHBA	0.14 (0.01)	0.13 (0.02)	0.33 (0.02)	0.44 (0.01)
BHT	0.00 (-[a])	0.00 (-)	0.83 (0.04)	38.22 (0.45)
BHA	0.57 (0.08)	0.00 (-)	3.12 (0.16)	12.54 (1.16)
BPA	0.00 (-)	0.20 (0.04)	2.31 (0.12)	10.99 (0.74)
DES	0.07 (0.01)	0.19 (0.03)	1.82 (0.34)	3.23 (0.29)
E1	0.00 (-)	1.31 (0.38)	5.68 (0.55)	20.61 (3.96)
E2	0.00 (-)	0.00 (-)	3.79 (0.26)	28.82 (2.37)
E3	0.00 (-)	0.00 (-)	3.98 (0.51)	31.80 (2.23)
EE2	0.00 (-)	0.00 (-)	3.01 (0.31)	27.66 (1.74)
OPP	0.00 (-)	0.21 (0.03)	1.75 (0.19)	4.73 (0.52)
TCS	0.37 (0.02)	0.33 (0.01)	0.86 (0.06)	0.53 (0.02)
TCC	0.41 (0.03)	1.33 (0.08)	2.23 (0.48)	2.91 (0.07)
4-T-OP	0.58 90.10)	0.00 (-)	5.18 (0.84)	16.92 (2.19)
4-N-NP	0.00 (-)	0.00 (-)	3.12 (0.37)	21.05 (1.87)

a -: not applicable

Table S5: Calibration equations, linear ranges (μg L^{-1}), intra-day and inter-day precision expressed by relative standard deviation (RSD, %) for both instruments (low concentration at 10 μg L^{-1} and high concentration at 200 μg L^{-1}, A: LC-QqQ-MS system and B: LC-Q-Orbitrap-HRMS system).

TOrCs	System A						System B					
	Equation	Linear Range (μg L^{-1})	Intra-day RSD (%)		Inter-day RSD (%)		Equation	Linear Range (μg L^{-1})	Intra-day RSD (%)		Inter-day RSD (%)	
			Low	High	Low	High			Low	High	Low	High
MEP	Y = -0.795617 + 2.06016*X	2.5-1000	1.2	0.7	3.7	3.6	Y = -0.0306051 + 0.0166368*X	0.5-500	5.6	3.4	6.5	2.7
ETP	Y = -1.52337 + 4.23122*X	2.5-1000	1.4	0.5	2.6	2.1	Y = 0.0260817 + 0.0154018*X	0.5-500	4.8	5.2	5.3	5.1
PRP	Y = -0.763601 + 3.03918*X	2.5-1000	1.5	0.9	2.8	2.6	Y = 0.00464969+0.0158108*X	0.25-500	4.0	5.7	6.8	2.4
BUP	Y = -2.61889 + 4.23974*X	2.5-1000	3.5	4.8	5.1	4.1	Y = 0.0157486 + 0.0196768*X	0.25-500	3.1	0.5	1.1	1.7
BEP	Y = -6.65782 + 4.10856*X	2.5-1000	0.9	1.1	2.9	2.2	Y = -0.00395942 + 0.0157598*X	0.25-500	5.3	2.3	3.6	1.0
HEP	Y = -19.7634 + 7.1285*X	2.5-1000	1.1	1.0	3.5	3.5	Y = 0.0098253 + 0.0289543*X	0.25-500	6.8	4.7	10.3	8.1
PHBA	Y = 1.1866+0.468575*X	5-1000	4.7	3.6	8.9	6.7	Y = 0.0268806 + 0.00798267X	0.55-500	3.1	1.9	10.8	2.5
BHA	Y = -3.21332 + 1.47844*X	2.5-1000	2.3	2.2	9.1	4.4	Y = 0.0242549 + 0.00775323*X	0.25-500	4.8	3.2	2.8	6.9
BHT	Y = -4.87434 + 1.12163*X	10-1000	7.0	4.5	8.9	5.6	Y = 0.0674911 + 0.0106836*X	1-500	9.0	4.8	9.4	3.1
OPP	Y = 13.2642 + 1.93125*X	1-1000	5.8	4.0	3.2	6.5	Y = 0.044005 + 0.00929338*X	0.1-500	3.0	2.7	1.7	8.1
TCS	Y = 22.0288 + 0.771564*X	2.5-500	2.1	0.6	1.9	3.0	Y = -0.00834042 + 0.0083841*X	0.1-500	8.7	4.8	10.0	9.5
TCC	Y = 8.93904 + 1.37486*X	0.5-500	5.0	0.7	2.7	2.5	Y = 1.20541 + 0.0539395*X	0.1-500	9.0	5.4	13.1	2.3
BPA	Y = -6.48541 + 4.34624*X	1-1000	4.2	1.0	2.2	6.1	Y = -0.0550386 + 0.0149069*X	0.25-250	7.2	5.8	10.3	8.2
DES	Y = -5.12662 + 0.655379*X	2.5-1000	3.7	1.5	4.5	2.4	Y = 0.00948498 + 0.0126452*X	0.25-500	11.0	4.3	13.2	6.2
E1	Y = 1.62034 + 1.46164*X	5-1000	2.5	1.6	9.1	6.8	Y = 0.0267467 + 0.00786257*X	0.25-500	10.5	4.6	5.6	7.0
E2	Y = -0.701054 + 1.9572*X	1-1000	5.5	2.9	8.2	4.5	Y = 0.0109521 + 0.00830575*X	0.25-500	2.1	3.4	2.6	0.8
E3	Y = 5.34072 + 1.67395*X	1-1000	4.5	3.6	9.3	7.7	Y = 0.00473618 + 0.0064804*X	0.5-500	10.7	5.8	12.3	8.5
EE2	Y = -1.56431 + 1.70618*X	2.5-1000	4.3	2.4	11.8	5.7	Y = -0.0146325 + 0.0111053*X	0.25-500	9.9	4.7	7.0	8.3
4-t-OP	Y = -5.28883 + 0.651247*X	2.5-1000	3.5	2.5	8.5	6.7	Y = 0.0382851 + 0.0151435*X	0.5-500	1.2	3.8	11.8	2.1
NP	Y = 1.95013 + 1.03056*X	1-1000	4.2	2.2	11.7	8.1	Y = 0.0113376 + 0.014285*X	0.5-500	6.9	8.4	8.0	3.8

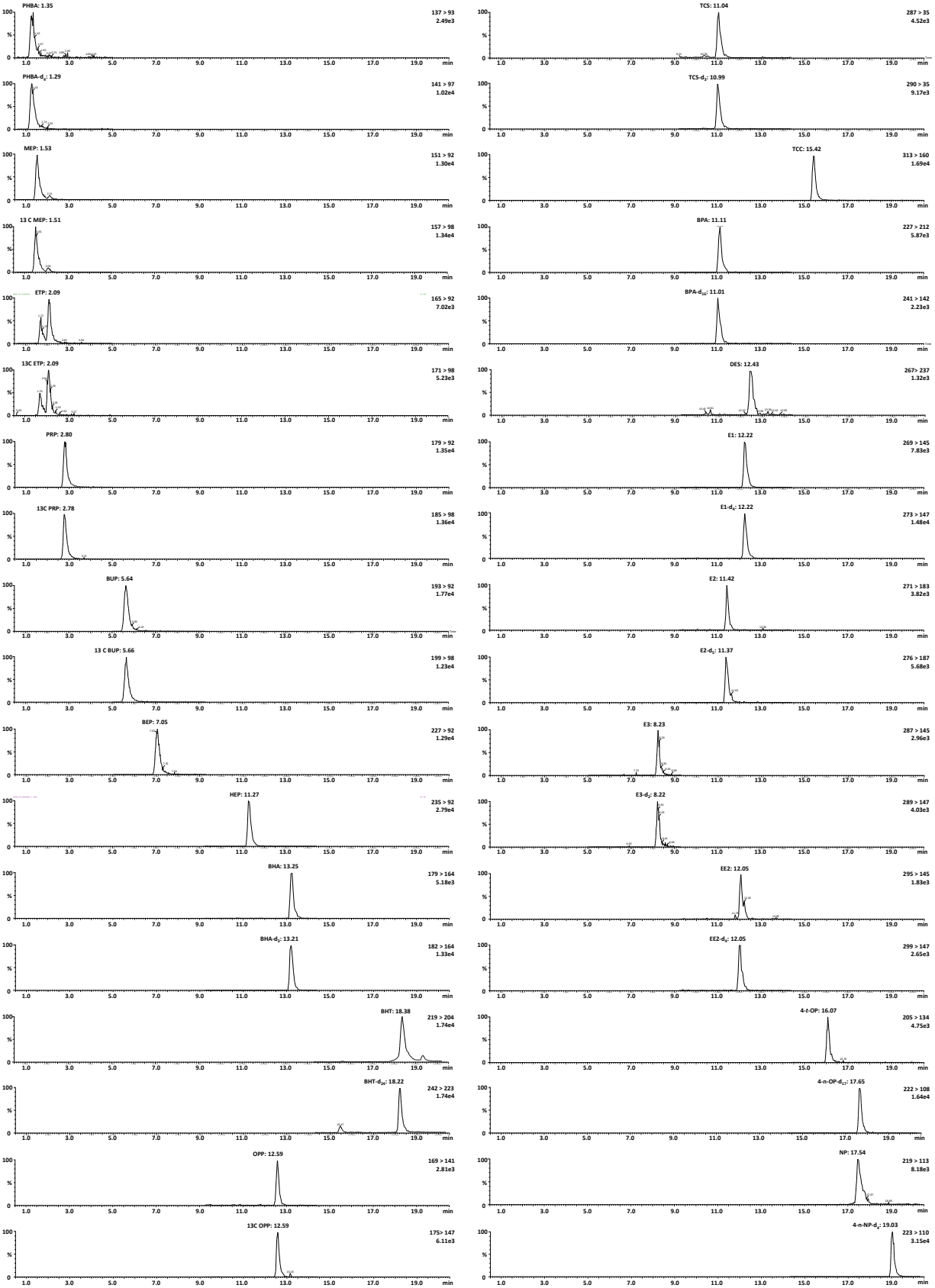


Figure S1: Extracted ion chromatograms (EIC) of the quantitative ions for TOrCs and ISs (100 ng L^{-1}) in river water analysed by LC-QqQ-MS.

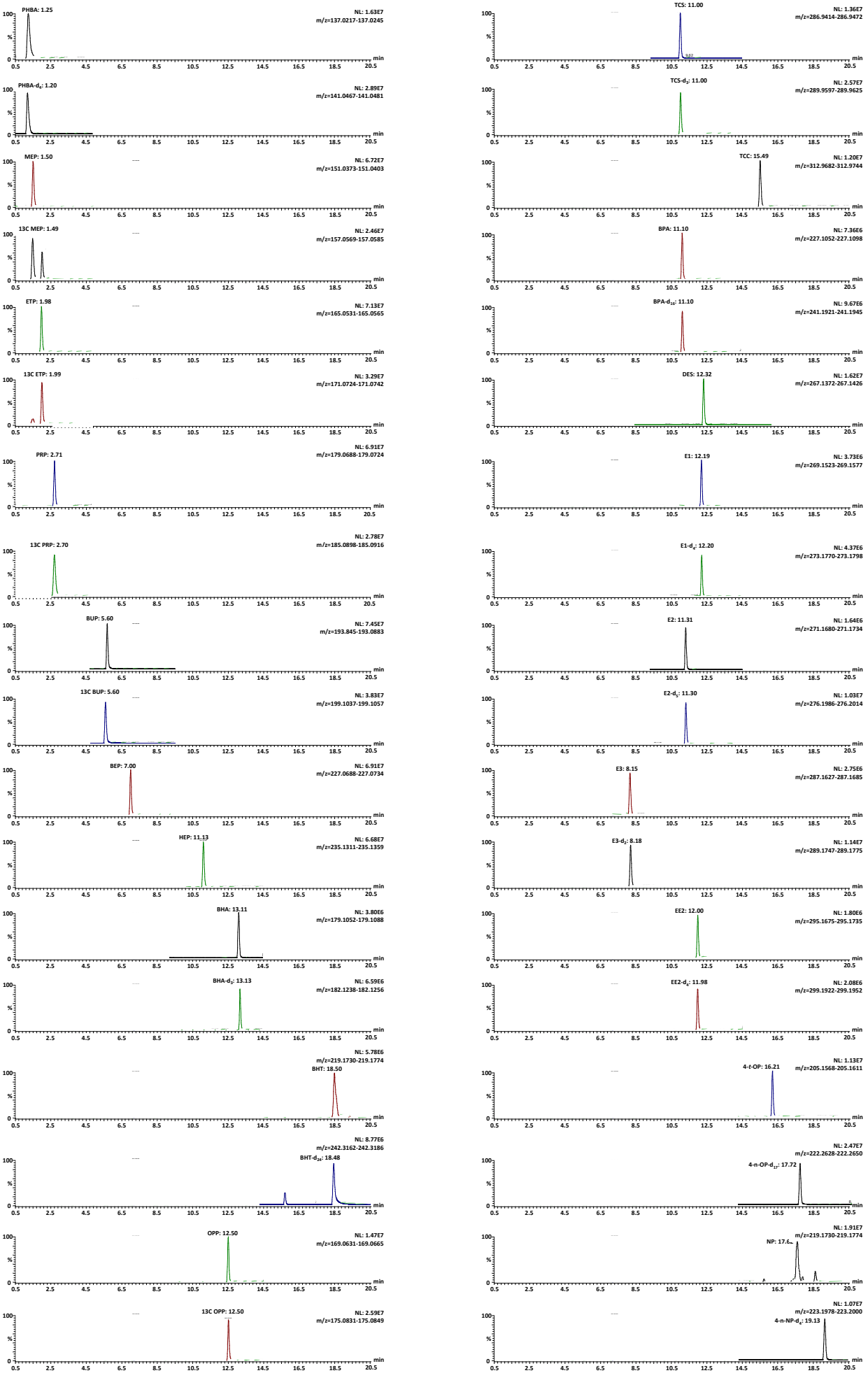


Figure S2: Extracted ion chromatograms (EIC) of the quantitative ions for TOrCs and ISs (100 ng L^{-1}) in river water analysed by LC-Q-Orbitrap-HRMS.

Paper IV

Validation of DGT Technique for Trace Organic Chemicals in Waters

Validation of DGT Technique for Trace Organic Chemicals in Waters

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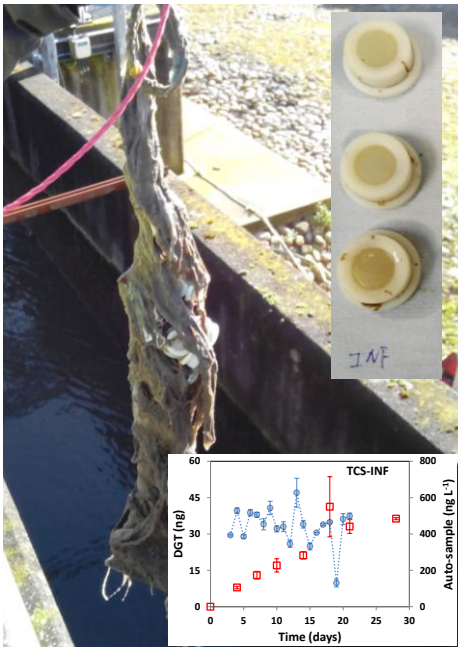

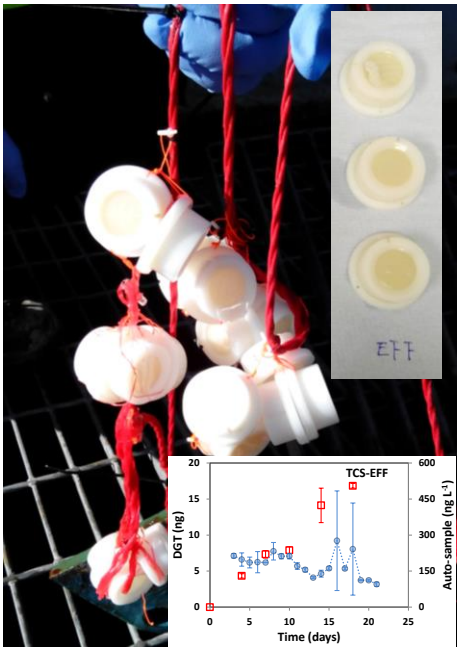

ABSTRACT

A novel passive sampler based on DGT technique for selected trace organic chemicals (TOrCs) has previously been developed and tested in the laboratory. Here we test the sampler performance in the field at a British wastewater treatment plant (WWTP). Raw influent and final effluent were sampled over up to 28 days, using DGT samplers, active auto-samplers and grab sampling methods. Twenty TOrCs, including preservatives, antioxidants, disinfectants, oestrogens and alkyl-phenols, were analysed by liquid chromatography-tandem mass spectrometry (LC-MS/MS). The majority of 20 TOrCs were detected in DGT samplers, and the accumulation in the DGT typically started to plateau after 18 days, probably due to the effect of the co-existing substances and biofouling. The effect of the diffusive boundary layer (DBL) was estimated *in situ*, showing the DBL thickness was 0.25 and 0.07 mm in the influent and effluent, respectively, which is relatively limited compared with other passive samplers for organics. The sampling rate per unit exposure area of DGT was comparable with other similar passive samplers. The DGT sampler compared well with the auto-samplers, integrating concentrations over the deployment period in a way that grab-sampling obviously does not. The DGT sampler has advantages in terms of cost, ease of simultaneous multi-site deployment, *in situ* pre-concentration and reduction of matrix interferences comparing with conventional methods. This passive sampler could constitute an alternative to conventional active water sampling for routine monitoring of TOrCs and for studying their fate and behaviour in the aquatic environment.

1. INTRODUCTION

Passive approaches to sampling chemicals from waters has been widely developed and exploited over last few decades,[1] providing advantages over conventional water sampling for trace compounds in the aquatic environment.[2] Dynamic kinetic passive sampling[3, 4] can provide time-weighted average (TWA) concentrations of target compounds in water and could be more effective regarding time, labour and costs.[5] It can help analytically too by being an *in situ* analyte pre-concentration step and reduce/eliminate the matrix interferences,[6] but few studies have presented the quantitative evidence of this advantage. The polar organic chemical integrative sampler (POCIS) and Chemcatcher have been used for various polar organic contaminants in waters.[2, 7, 8] However, one major drawback of these samplers is that *in situ* and/or laboratory calibration is required to provide reliable results, because their designs are flow-rate dependent.[2, 9, 10]

Recently, the diffusive gradients in the thin films (DGT) technique, which has been widely used and validated for a wide range of inorganic contaminants,[11] has been developed and tested for antibiotics,[5, 12] and then configured and tested for *in situ* measurement of phenolic compounds[13-15] and a pesticide and its metabolite[16] in the water. The principle of DGT is that target compounds diffuse through a thin (~ 1 mm) diffusion layer and accumulate to the binding layer. This process is solely controlled by molecular diffusion,[11] thus the effect of the diffusive boundary layer (DBL) is less important or could be neglected compared with the diffusive gel.[17] This sampler is relatively flow-rate independent, except under very still water conditions.[12, 17, 18]

The widespread application of TOrCs has resulted in their detection in the aquatic ecosystem, and become increasing concerned.[19] Monitoring the concentrations of TOrCs is needed for

studying their fate and behaviours in aquatic environments and for further assessing their potential risks/toxicity on ecosystems and human health. Conventional sampling methods, such as grab-sampling and auto-sampling, encounter some problems in terms of cost, representation of samples and effects of complex matrix in the samples. Thus, DGT sampler could potentially provide a good alternative to both overcome the imperfection and fulfil the need.

It is known that DGT will sample the labile/free concentration of chemicals and that it gives a TWA concentration, up to the point its capacity is reached. A novel passive sampler based on DGT technique for selected trace organic chemicals (TOrCs) has previously been developed and tested in the laboratory.[18] The aim of this study was therefore to test the performance of this DGT sampler in challenging real-world conditions at a wastewater treatment plant (WWTP). We deployed DGT devices alongside conventional active samplers and grab sampling. DGT performance was assessed for different deployment times. We investigated the effect of DBL on sampling in the field, and made assessments on compound detection when combining DGT with liquid chromatography-tandem mass spectrometry (LC-MS).

2. MATERIALS AND METHODS

2.1 Chemical and Reagents

Twenty high purity standards of TOrCs were purchased from Sigma-Aldrich (UK). The range covered six preservatives and one of their metabolites, two antioxidants, three disinfectants, six oestrogens and two alkyl-phenols, as follows: methylparaben (MEP), ethylparaben (ETP), propylparaben (PRP), butylparaben (BUP), benzylparaben (BEP), heptyl paraben (HEP) and 4-hydroxybenzoic acid (PHBA), butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), ortho-phenylphenol (OPP), triclosan (TCS), triclocarban (TCC), bisphenol-A (BPA),

diethylstilbestrol (DES), estrone (E1), *β*-estradiol (E2), estriol (E3), 17*α*-ethinylestradiol (EE2), 4-*tert*-octylphenol(4-*t*-OP) and nonylphenol (NP). The properties of these TOrCs are listed in the Supporting Information (SI) **Table S1**. The internal standards (ISs) were purchased from Sigma-Aldrich (UK), including ^{13}C MEP, ^{13}C BUP, ^{13}C PRP, ^{13}C BUP, BHA-d_3, ^{13}C OPP and BPA-d_{16}. Other ISs were purchased from QMX Laboratories (UK): PHBA-d_4, BHT-d_{24}, TCS-d_3, E1-d_4, E2-d_5, E3-d_2, EE2-d_4, 4-n-OP-d_{17} and 4-n-NP-d_4.

Water used in the study was supplied from a Milli-Q water (MQ water) purification system (>18.2 MΩ cm^{-1}, Millipore, UK). Regents are at least analytical reagents with ≥ 99% purity, organic solvents are HPLC grade. Ammonia solution (NH_4OH, 5 M) was purchased from Sigma-Aldrich (UK). Hydrochloric acid (HCl, 35.5-37.5 %), methanol (MeOH), acetonitrile (ACN) and ethyl acetate (EA) were obtained from Fisher Scientific (UK).

2.2 DGT and Active Sampling

The DGT devices with HLB resins as binding gels were deployed *in situ* in the influent and effluent at a WWTP of UK (freely dangled at about 30 cm below the water surface). The DGT samplers were produced as described previously.[18] In brief, DGT devices containing a HLB binding gel (0.4 mm), an agarose diffusive gel (various thicknesses) and a polycarbonate membrane (PC filter, 0.01 mm, track-etch membrane, Nuclepore, Whatman) between the plastic DGT base and cap, with an exposure area of 3.14 cm^2 were prepared. The standard DGT devices (with 1 mm diffusion layer) for time series analysis were deployed for up to 28 days, and retrieved in triplicate after 4th, 7th, 10th, 14th, 18th, 21st and 28th days, to investigate the effect of deployment time, possible interferences and competitions from other chemicals. All the 28 days' samples in the influent were retrieved, but samples after 18 days in the effluent were lost due to the turbulent flow. A separate study of DGT devices prepared with different thicknesses of

diffusive gels (0.35, 0.5, 1, 1.5 and 2 mm) and deployed at the same sites for 8 days, was conducted to estimate the DBL thickness at the sites.

Active sampling for auto-samples and grab-samples were also undertaken at both influent and effluent sites in the WWTP. Weather-refrigerated automatic samplers (SIGMA SD900) were installed to collect the influent and effluent in the WWTP. They were set on the consistent flow mode (~100 mL h^{-1}) to provide a 24-hour composite water sample (auto-sample, 2.4 L/sample) daily for 3 weeks. Auto-samples were not collected for the first two days due to the technical problems. Grab samples were collected at about 10 am every first and last day of the week of the DGT deployment, using 1 L pre-cleaned amber bottles. The water temperature, pH and weather conditions were recorded when samples were taken. The range of temperature in the influent and effluent was 8.5-10.9 ℃ (average 10.0 ℃) and 8-10.3 ℃ (average 9.3 ℃), respectively; and the pH was 6.9-7.2 (average 7.0) and 7.1-7.4 (average 7.3) in the influent and effluent, respectively.

2.3 Sample Extraction and Instrumental Analysis

Extraction of DGT samples were as described previously.[18] In brief, the resin gel was taken from the retrieved DGT sampler and placed in a clean amber sample vial. 5 mL of ACN was added to the vial to extract the TOrCs from the resin gel. 100 ng of ISs was added before extraction. The vials were placed into an ultrasonic bath for 30 minutes extraction. Extraction of water samples (both auto-samples and grab-samples) was based on the solid-phase extraction (SPE) method optimised according to previous literature.[20] Briefly, 500 mL water samples were acidified, filtered and spiked with ISs (100 ng), and then loaded using Supel-Select HLB tubes (200 mg. 6 mL) preconditioned with 10 mL mixture of EA and ACN (50 % : 50 %, v/v) and 10 mL MeOH

119 followed by 10 mL MQ water. After loading, the TOrCs held on cartridges were finally eluted
120 with 12 mL of the mixture solvent.

121 Both DGT and active sample extracts were then reduced to about 1 mL under a gentle flow of N_2.
122 They were then syringe filtered (0.22 μm, PTFE, Whatman) into amber vials and stored at -20 ℃
123 until liquid chromatography-tandem mass spectrometer (LC-MS/MS) analysis. The details of the
124 sample pre-treatment and instrumental analysis are provided in the **SI**.

125 ## 2.4 TWA Concentrations Measured by DGT

126 The TWA concentrations of TOrCs measured by DGT in the water (C_{DGT}) was calculated by
127 Equation (1):[11]

128 $$C_{DGT} = \frac{M(\Delta g + \delta)}{D_e A t} \text{ or } C_{DGT} = \frac{M\Delta g}{D_e A t} \quad (1)$$

129 where M is the measured mass of target chemical accumulated in the binding gel, Δg is the
130 thickness of the diffusive layer, δ is the thickness of DBL, D_e is the diffusion coefficient of target
131 chemical and t is the exposure time and A is the exposure window area of cap. Δg is typically
132 much thicker than the thickness of DBL under most conditions, so that the influence of the DBL
133 becomes negligible,[11, 17] and the C_{DGT} could be simply calculated using the latter version of
134 Equation (1). D_e of target chemicals was measured at 25 ℃ using a diffusion cell, D_e at other
135 temperature could also be calculated.[18]

136 ## 2.5 Quality Control and Quality Assurance (QA/QC)

137 Blank and control water samples (MQ water and MQ water with 100 ng TOrCs spiked) and
138 blank DGT samples were analysed to assess potential contamination and loss. Recoveries of

TOrCs from wastewater were determined by spiking TOrCs (100 ng L^{-1}) into the influent. Values ranged from 59.4 to 125 % (see **Table S2**). The instrumental detection limits (IDLs) of TOrCs were calculated based on the 3 times of signal-to-noise values (S/N) and method detection limits (MDLs) were calculated based on IDLs, the concentration factors and the absolute recoveries for water samples and DGT samples, which results were listed in **Table S2**.

3. RESULTS AND DISCUSSION

3.1 Detection and Uptake of TOrCs by DGT

Among the 20 analysed TOrCs, only BEP was lower than MDL in auto-samples from the influent during the whole 3-week period, HEP, BHA, DES and NP were not detected in some days, and all other 16 TOrCs were detected every day. In the effluent, more TOrCs were not detected even once at all, which included BUP, BEP, HEP and E2; some other TOrCs like PRP, DES, E3 and NP were partly detected in some days; and other 12 TOrCs could be detected for all 3 weeks. Similar results were found in the grab-samples and relatively more compounds were not detected, indicated the grab-sampling method missed the peak/discharge of these chemicals in the wastewater. For DGT samples, BEP, HEP, DES, E2 and EE2 were not detected in the influent over the 28-day period. Other 15 compounds could be detected more than once by DGT in the influent. PRP, BUP, BEP, HEP, BHT, DES, E2 and EE2 were not detected in the DGT samples at the effluent, the other 12 TOrCs could be detected at least once in DGT deployed in the effluent.

Most TOrCs detected in the DGT samples continually accumulated in the binding gels from the wastewater for about 18 days, with the exception of PHBA and 4-*t*-OP in the influent and PHBA in the effluent (**Figure 1** gives some examples for typical TOrCs and the full sets of data can be

found in **Figure S1**). In the influent, only BPA and TCC continue accumulating up to 28 days, while other detected TOrCs in DGT reached the plateaus or started to decline after 18 days.

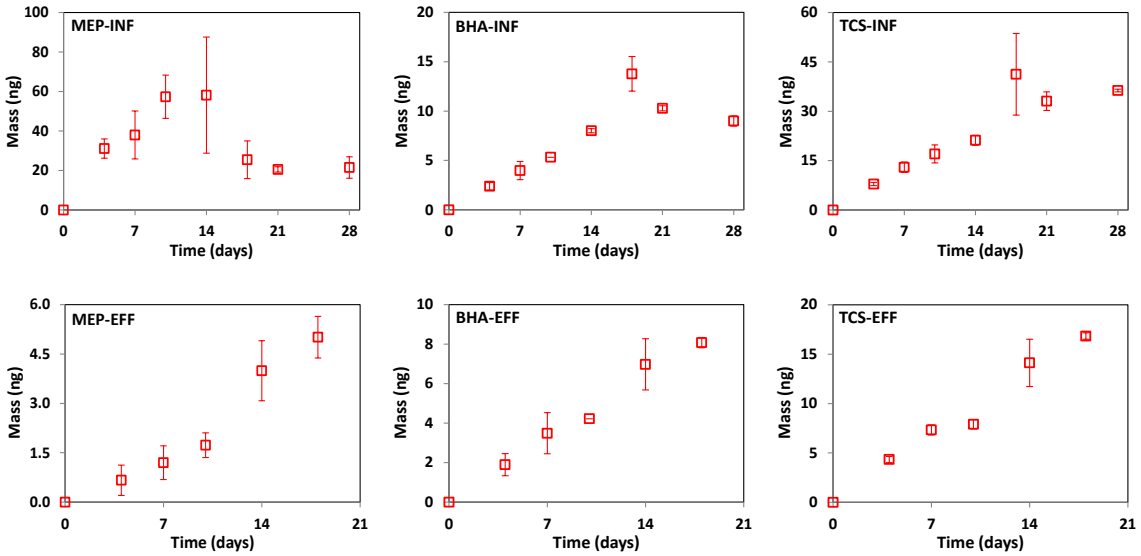

Figure 1. Uptake of typical TOrCs by DGT (n=3, INF: influent, EFF: effluent) in the wastewater of a British WWTP. Error bars were calculated from the standard deviation (SD) of three replicates.

Not all detected TOrCs could be found after 4 days' deployment in both influent and effluent. A 7-18 day deployment resulted in detection of most detected TOrCs in DGT and the operation of sampler in the linear uptake phase (**Figure S1**). Similar phenomenon was observed when DGT and POCIS were used to sample for antibiotics and drugs in WWTPs,[5, 21] the plateau or decline were found after a period of accumulation. There would appear to be 3 possible reasons for a reduction in sampling rate or decline in mass retained on the resin gel-namely biofouling, degradation of TOrC happened on the resin, or the uptake and retention of co-existing/competing substances. Biofouling will affect sampling rate (by adding to the layer the TOrCs need to diffuse through and/or by degrading TOrC in the bio-layer), while the latter 2 factors would

result in a reduction in the mass of TOrC retained. Differences in compounds properties will influence their susceptibility to degradation.

3.2 DBL Effect and Sampling Rate

The thickness of DBL varies with water flow rates. As DBL is a compound-independent physical parameter, the thickness of the DBL should be the same for all target TOrCs, for a given flow rate. If the effect of the DBL is negligibly small, the measured mass of TOrCs in a given time by DGT should be inversely proportional to the thickness of the diffusive gel layer (according to the latter version of Equation (1)). If the δ is significant when compared to Δg, the plot of M versus $1/\Delta g$ will be nonlinear. To determine the *in situ* DBL thickness (δ), the following Equation (2)[11] that derived from Equation (1) can be used.

$$\frac{1}{M} = \frac{\Delta g}{D_e C_{DGT} A t} + \frac{\delta}{D_e C_{DGT} A t} \quad (2)$$

The DGT devices with various thicknesses of diffusive gel layer were deployed at the same time for the same length of deployment time. Reciprocal of accumulated masses of TOrCs ($1/M$) was then plotted against the thickness of the diffusive layer (Δg). **Figure 2** gives some examples, while others are given in **Figure S2**. The δ can then be calculated using the ratio of the intercept and the slope of the regression line.

The results shows the DBL thickness for the influent and effluent was in the range from 0.20 to 0.29 mm (mean 0.25 mm) and from 0.05 to 0.09 mm (mean 0.07 mm), respectively. The average DBL thickness in the influent was 0.25 mm, which was less than the determined in unstirred solution for TOrCs and more than in slowly stirred solution (100 rpm) for TOrCs,[18] and very similar with a previous study conducted at the same site of the same WWTP.[5] The average

thickness of DBL in the effluent was 0.07 mm, which was similar with the result for TOrCs in the well-stirred solution.[18] The smaller DBL thickness in the effluent than in the influent was also consistent with the observation in the field: the more turbulent flow was in the final effluent, resulting in the loss of some of the DGT deployed at this site. All DGT were retrieved successfully over the 28 days in the influent.

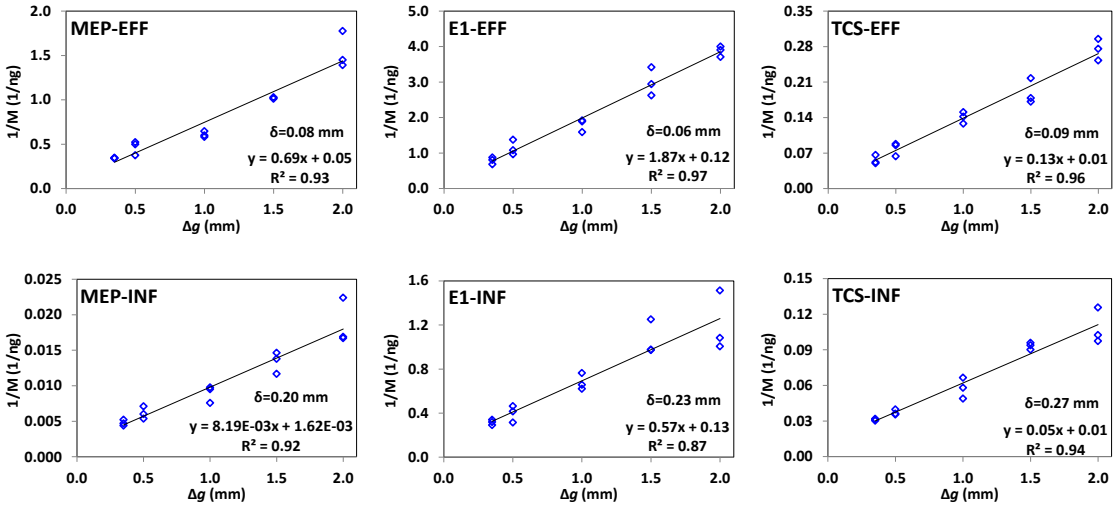

Figure 2. Plot of 1/mass (1/M, 1/ng) of typical TOrCs accumulated by DGT deployed in both influent (INF) and effluent (EFF) versus different diffusive gel thickness (Δg, mm).

To reduce the errors on the TWA concentrations, 0.25 and 0.07 mm were used as the DBL thicknesses when calculating the C_{DGT} in the influent and effluent in this study, respectively. If the DBL effects were not considered when calculating the C_{DGT} for DGT devices with diffusive layer of 1 mm thickness, the TWA concentration will be about 20 % underestimated in the influent and only about 6 % underestimated in the effluent. The results indicate that the effects of DBL are relatively small for DGT sampler, the effect should be only considered when DGT devices were deployed in the water with very slow flow rate or still water. Comparing with DGT sampler, other passive samplers for organics like POCIS and Chemcather, the effect of DBL will

be much greater, which will produce several-folds errors on sampler measured concentrations for these samplers with different water flow rates.[2]

Sampling rate (R_S) was essential for evaluating the effectiveness of some passive sampling devices.[2] For POCIS and Chemcatcher, R_S was normally measured or calibrated using laboratory or field data and then used to calculate the TWA concentrations. Although the R_S was not used when calculating the TWA concentrations for DGT sampler, the R_S could be estimated using Equation (1) for comparison purpose:[12]

$$R_S = \frac{D_e A}{\Delta g} \quad (3)$$

Due to the different designs and exposure areas among the passive samplers, it is not reasonable to directly compare the R_S for different samplers. Therefore, the normalised R_S, the sampling rate per unit area ($R_{S/A}$) was calculated for comparison of the R_S for all types of samplers. For DGT sampler, the $R_{S/A}$ could be estimated by Equation (4) below;[5] and $R_{S/A}$ could be calculated by latter version of Equation (4) for POCIS and Chemcatcher:

$$R_{S/A} = \frac{D_e}{\Delta g} \text{ or } R_{S/A} = \frac{R_S}{A} \quad (4)$$

The $R_{S/A}$ of TOrCs for standard DGT (1 mm diffusion layer) were calculated using D_e at 25 ℃ of individual chemicals measured using a diffusion cell (**Table S3**) and $R_{S/A}$ for POCIS and Chemcatcher were also calculated using available data on R_S of these TOrCs for POCIS and Chemcatcher (data are listed in **Table S3**). It could be found that the values of $R_{S/A}$ for DGT at 25 ℃ were ranged from 2.90 to 6.31 mL (d cm^2)$^{-1}$, which were similar range with POCIS and Chemcatcher. Take BPA for example, calculated $R_{S/A}$ for DGT, POCIS and Chemcatcher was

4.14, 6.78 (ranged from 1.92 to 19.05) and 6.54 mL (d cm^2)$^{-1}$, respectively. This indicated DGT could provide comparable data with POCIS and Chemcatcher.

3.3 Comparison of DGT Measurement and Active Sampling Methods

3.3.1 Performance

To compare the performance between the DGT and active sampling methods, the average concentrations were calculated. **Figure 3** gives an example for the average concentrations for 7-day sampling, the full set of concentrations for 4, 10, 14, 18, 21 and 28-day sampling could be found in **Figure S3**. For most detected TOrCs by DGT, their concentrations are similar to the concentration obtained by auto-sampling. For individual TOrCs detected by the DGT, the concentrations obtained for different deployment time are also agreed well with the average concentrations of auto-samples (**Figure S4**). The similar results between DGT measurement and auto-sampling concentrations indicated that DGT could provide continuous TWA data in the wastewater, comparable with auto-sampling method.

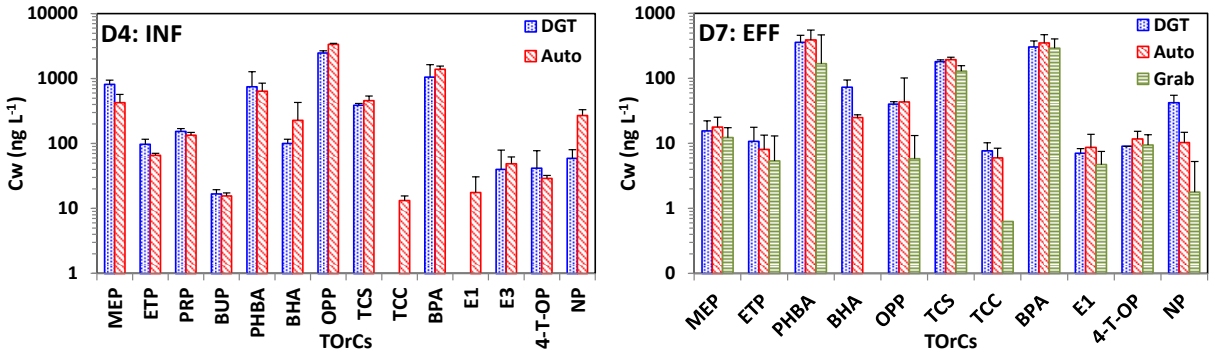

Figure 3. 7-day TWA concentrations of DGT samples (n = 3) and average concentrations of auto (n = 10) and grab (n = 4) samples for compounds detected by DGT in influent and effluent, error bar: 1 standard deviation.

However, there was slight difference between the concentrations obtained by the two methods, with lower values for DGT in most cases. Similar results were found in the previous study on

antibiotics between the DGT and auto-sampling.[5] This could be probably explained by differences of the ionizability and fractions of compounds in collected by both samples and co-existing substances in the samples: DGT is an *in situ* technique for sampling free dissolved fraction of chemicals without changing the any water properties, while the auto-samples in this study were pre-treated by SPE after pH adjustment (for better recoveries, pH 2.5) and filtration (0.7 μm). The values of pH for the natural wastewater were about 7.0-7.3 in this study, while the water pH ready for SPE was 2.5, this will lead more neutral fraction in the auto-samples, resulting in the higher concentrations in the auto-samples. The auto-samples will also contain some particles besides the free dissolved fraction, while the DGT will only sample the free dissolved fraction. As mentioned in the Section of ***Detection and Uptake of TOrCs by DGT***, the co-existing substances could also affect the uptake of TOrCs in the DGT, leading to lower concentrations were detected. Grab sample results are not was not always consistent with the DGT and auto-sample results. It is well known that grab samples miss any special events during the sampling period, such as the peak, point source, rain or discharge events (or only record these events inversely).[22]

3.3.2 Increased sensitivity of DGT measurement

Two significant virtues of the DGT sampler for trace organic analysis are that it can pre-concentrate compounds *in situ* and it can reduce matrix interferences. To illustrate this, if DGT is deployed for 14 days, it would sample ~ 200 mL of water. If this is transferred to 1 mL of solvent, so that a sub-sample can be injected into LC-MS, this represents a 200-fold pre-concentration. Obviously this ratio can be adjusted to further concentrate, by deploying replicate DGT devices and concentrating as a single sample and smaller solvent volume can be attained, making pre-concentration of 3-4 magnitude achievable.

The reductions in matrix interference are apparent from the total ion chromatograms obtained in selected ion monitoring (SIM) (see **Figures S5 A and B**). Many more non-target peaks could be detected in the extract from auto-sample than that the DGT extract. When only one target ion was selected, more interference peaks could be were apparent in the auto-sample extract than that in the DGT extract. **Figures S5 C and D** give an example for *m*/*z* 151, the target ion of MEP.

3.4 Perspectives and Potential Applications

This study confirmed that DGT sampler could provide reliable measurement for TOrCs in field conditions, as the DGT devices could continuously accumulate TOrCs for 18 days. The $R_{S/A}$ was comparable with other passive samplers, such as POCIS and Chemcatcher. Considering the lower detection limits and the less fouling effects, 1 or 2 weeks deployment will be recommended for practical application and two different periods of deployment should be conducted to check the kinetic uptake of the sampler throughout the deployment. This DGT sampler was less dependent on the water flow rate than other similar passive samplers. The thickness of the DBL can be estimated by deploying DGT devices with different diffusive gels thicknesses simultaneously. Good agreement between DGT measurements and auto-sampling concentrations proved that DGT could be an alternative approach to conventional active water sampling for studying the fate and behaviour of TOrCs in the aquatic environment. Additionally, some potential applications of DGT could be recommended according to the virtues demonstrated in this study:

1. DGT sampler could be used as a tool to assess the chemical removal efficiency in WWTPs, as it could provide reliable TWA concentrations easily, while the grab-sampling may miss the peak/discharge events. Auto-sampling devices may not be available at most sites due to their

high cost. The total removal efficiency (*Removal*, %) of the TOrCs in the WWTP of this study could be roughly estimated using the Equation below (5):

$$Removal = \frac{C_{\text{inf}} - C_{\text{eff}}}{C_{\text{inf}}} \times 100\% \quad (5)$$

where C_{inf} and C_{eff} are the TWA TOrC concentrations measured by DGT in the influent and effluent, respectively. When using the 7-day DGT concentrations, the overall removal efficiencies were ranged from 24 to 100 %, which are very similar (26 to 100 %) with the results calculated using the 7-day average concentrations of auto-samples.

2. The DGT sampler could be used for screening of illegal discharge of industrial compounds in aquatic environment, as this sampler provides TWA concentration and will not miss any discharge events during the deployment. It also could be applied for the target or non-target screening of emerging contaminants and their metabolites in aquatic environment, as it could be able to increase the sensitivity of the measurements through *in situ* pre-concentration and also could reduce matrix interferences for analysis, and the relatively long sampling period (short-term for grab-sampling and about 24 h for auto-sampling, but about 1 week for DGT) will access and record the biotransformation process of the metabolites.

3. This DGT sampler could also be potentially applied for bioavailability of emerging contaminants by simplifying the procedures and reducing the use of animal tests. Many studies have conducted on metals bioavailability using the DGT to model the uptake by plants from soil and few studies on organics using the DGT.[23-25]

Overall, DGT could be a promising tool for investigating the fate and behaviours of emerging contaminants, especially for polar organic pollutants in aquatic environment, and also have strong potentials in many aspects of environmental applications.

ASSOCIATED CONTENT

Supporting Information

Water and DGT sample pre-treatment, instrumental analysis, diffusive coefficients (D_e) and sampling rate per unit area ($R_{S/A}$) for target compounds, TOrCs uptake in DGT and water concentrations for detected TOrCs, physical-chemical properties of TOrCs used in this study, the detection limits of for active and DGT sampling. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declared no competing financial interest.

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Supporting Information for

Validation of DGT Technique for Trace Organic Chemicals in Waters

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Water and DGT sample pretreatment

Water samples were firstly adjusted to pH=2.5 (2 M HCl) and filtered through a GF/F filter (47 mm, 0.7 μm) to remove the suspended particles and then divided into duplicate samples (500 mL each). 100 ng of individual internal standards were also added into filtered samples before extraction. The Supel-Select HLB tube (200 mg, 6 mL) was preconditioned with 10 mL mixture of EA and ACN (50 % : 50 %, v/v) and 10 mL MeOH followed by 10 mL MQ water, and the water samples were then introduced into the cartridge at a flow rate of about 3 mL min^{-1}. After the water sample passed, the sample bottle was rinsed twice with two aliquots of 50 mL of 5 % (v/v) methanol in MQ water, which also passed through the cartridge. After loading, the cartridges were rinsed with 10 mL MQ water and vacuum dried for 20 min. The TOrCs held on cartridges were finally eluted with 12 mL the mixture solvent.

Once retrieval, the DGT holders were rinsed with MQ water thoroughly before disassembly. The filter and diffusive gel layer was peeled off, and the resin gel layer was placed in a clean and baked amber sample vial. 5 mL of ACN was added to the vial to extract the TOrCs from the resin gel. 100 ng of internal standards was added before extraction. The vials were placed into an ultrasonic bath for 30 minutes when extraction.

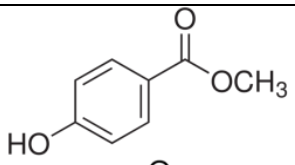
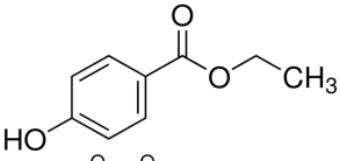
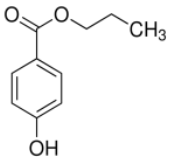
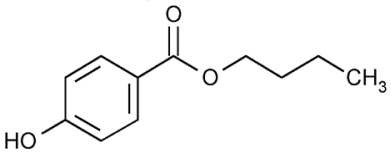
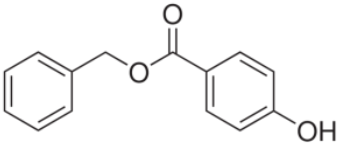
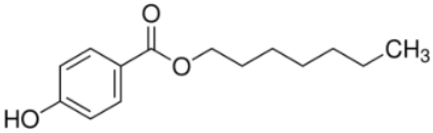
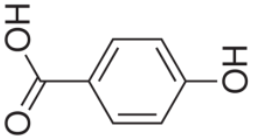
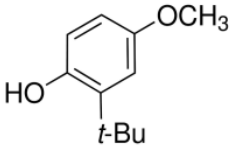
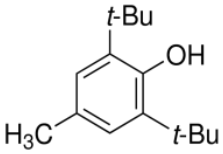
Both DGT and wastewater sample extracts were then blown to about 1 mL under a gentle flow of N_2, followed by syringe filtering (0.22 μm) to amber vials, stored at -20 ℃ waiting for liquid chromatography-tandem mass spectrometer (LC-MS/MS) analysis. Just prior to the LC-MS/MS analysis, 200 μL aliquot of each water sample extract (300 μL of DGT samples) were dried under a gentle N_2 flow and reconstituted in 50 μL of water and methanol mixture with 5 mM NH_4OH (50 % : 50 %, v/v).

Instrumental analysis

The target TOrCs were then analysed by LC-MS/MS following the method in our previous study:[1] LC separation was carried out on an Xbridge BEH C18 Column (100 mm × 2.1mm, 2.5 μm, Waters, UK) with a pre-column on an Agilent 1100 HPLC system. Mobile phase A: 95 % MQ water, 2.5 % ACN and 2.5 % MeOH with 5 mM NH_4OH; mobile phase B: 95 % ACN, 2.5 % MeOH and 2.5 % MQ water with 5 mM NH_4OH. The flow rate was 0.2 mL min^{-1} and the gradient procedure was optimised: the gradient began at 85 % A (equilibrium time 1 min), then decreased to 20 % A within 9 min, followed by reaching to 0 % A in 5 min, held for 4.5 min, after that increased to the initial condition (85 % A) in 0.5 min, finally, 10 min of post-run ensured re- equilibrium of the column before the next injection The injection volume was 10 μL and the column and the tray temperature were kept at 25 ℃ and 10 ℃, respectively.

A Quatro Micro triple-quadruple mass spectrometer (Micromass, Manchester, UK) equipped with an electrospray ionisation source was used to analyse TOrCs in negative mode for both wastewater and DGT samples. The MS parameters, including the capillary voltage of 3 kV, the source temperature of 120 ℃ and the desolvation temperature of 350 ℃ were optimised according to a previous study with the same mass spectrometer for similar compounds. The cone gas flow of 0 L h^{-1} and desolvation gas flow of 600 L h^{-1} were used and Argon (99.999%) was used as a collision gas. The mass spectrometry analysis was performed in the multiple reaction monitoring (MRM) mode. The quantifier ions and confirmation ions were also optimised according to previous studies. A nine-point response calibration ranged from 1 to 400 μg L^{-1} was established to quantify the target analyses using the internal standard method. The detection limits for the field samples were list in **Table S2**.

78 **Table S1:** Physical-chemical properties of TOrCs in this study[1].

Group	Chemical (Abbr.[a]), CAS number and purity	Molecular formula and weight	Water solubility (mg L^{-1})[e]	pK_a[c,e]	LogK_{OW}[d,e]	Structure
Preservative	Methylparaben (MEP) 99-76-3 ≥ 99.0%	$C_8H_8O_3$ 152.15	2500	8.31	2	
	Ethylparaben (ETP) 120-47-8 ≥ 99.0%	$C_9H_{10}O_3$ 166.17	885	8.50	2.49	
	Propylparaben (PRP) 94-13-3 ≥ 99.0%	$C_{10}H_{12}O_3$ 180.2	500	8.23	2.98	
	Butylparaben (BUP) 94-26-8 ≥ 99.0%	$C_{11}H_{14}O_3$ 194.23	207	8.50	3.47	
	Benzylparaben (BEP) 94-18-8 ≥ 99.0%	$C_{14}H_{12}O_3$ 228.25	23.419	8.49	3.70	
	Heptyl paraben (HEP) 1085-12-7 ≥ 99.0%	$C_{14}H_{20}O_3$ 236.31	8.022	8.50	4.94	
	4-Hydroxybenzoic acid (PHBA) 99-96-7 ≥ 99.0%	$C_7H_6O_3$ 138.12	5000	4.38 9.67	1.39	
Antioxidant	Butylated hydroxyanisole (BHA) 25013-16-5 ≥ 98.0%	$C_{11}H_{16}O_2$ 180.24	212.8	10.55	3.5	
	Butylated hydroxytoluene (BHT) 128-37-0 ≥ 99.0%	$C_{15}H_{24}O$ 220.35	0.6	11.60	5.03	

[1] This table is continued onto the next page.

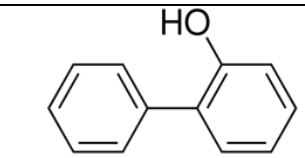
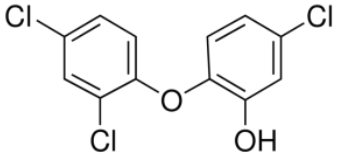
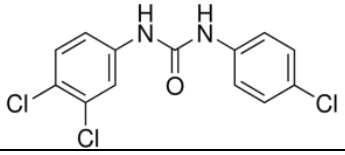
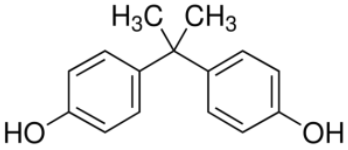
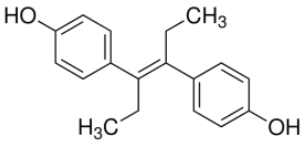
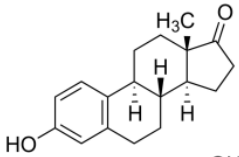
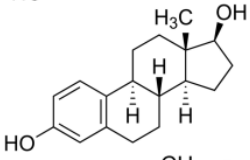
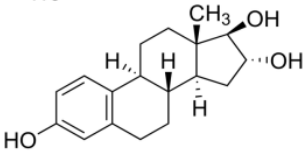
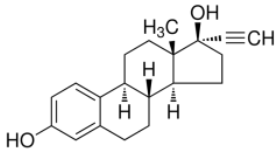
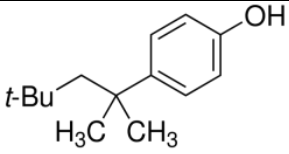
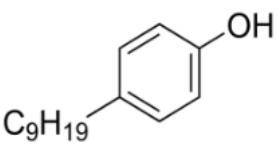
Group	Chemical (Abbr.[a]), CAS number and purity	Molecular formula and weight	Water solubility ($mg\ L^{-1}$)[e]	pK_a[c,e]	$LogK_{OW}$[d,e]	Structure
Disinfectant	Ortho-phenylphenol (OPP) 90-43-7 ≥ 99.0%	$C_{12}H_{10}O$ 170.21	700	9.65	3.28	
	Triclosan (TCS) 3380-34-5 ≥ 97.0%	$C_{12}H_7Cl_3O_2$ 289.55	10	7.68	4.66	
	Triclocarban (TCC) 101-20-2 ≥ 99.0%	$C_{13}H_9Cl_3N_2O$ 315.59	0.65	11.42	4.90	
Estrogen	Bisphenol-A (BPA) 80-05-7 ≥ 99.0%	$C_{15}H_{16}O_2$ 228.29	120	9.65 10.45	3.64	
	Diethylstilbestrol (DES) 56-53-1 ≥ 99.0%	$C_{18}H_{20}O_2$ 268.36	12	9.13 9.75	5.64	
	Estrone (E1) 53-16-7 ≥ 99.0%	$C_{18}H_{22}O_2$ 270.37	30	10.33	3.43	
	β-estradiol (E2) 50-28-2 ≥ 98.0%	$C_{18}H_{24}O_2$ 272.39	3.9	10.33	3.94	
	Estriol (E3) 50-27-1 ≥ 97.0%	$C_{18}H_{24}O_3$ 288.39	440.8	10.33 13.62	2.81	
	17α-Ethinylestradiol (EE2) 57-63-6 ≥ 98.0%	$C_{20}H_{24}O_2$ 296.41	11.3	10.33	4.12	
Alkylphenol	4-tert-octylphenol (4-t-OP) 140-66-9 ≥ 97.0%	$C_{14}H_{22}O$ 206.33	4.82	10.23	5.28	
	Nonylphenol (NP) 84852-15-3 analytical standard	$C_{15}H_{24}O$ 220.36	7.62	10.30	5.77	

Table S2: Average recoveries of TOrCs (%, (sd %)) in the spiked influent and the detection limits for active samples and DGT samples.

Chemical	IDL[a] (ng/ml)	Relative R[b] %, (n=3)	Absolute R[c] %, (n=3)	MDL[d] for active samples (ng L^{-1})[e]	MDL for DGT samples (ng/DGT)	MDL for DGT samples (ng L^{-1})[f]
MEP	0.88	92.1 (3.1)	82.2 (2.7)	0.54	0.15	1.14
ETP	2.47	97.4 (2.8)	90.5 (3.8)	1.37	0.41	3.40
PRP	1.22	103 (4.5)	88.0 (2.9)	0.69	0.20	1.82
BUP	1.47	87.8 (3.0)	87.9 (4.2)	0.84	0.24	2.32
BEP	2.24	148 (4.5)	98.5 (9.6)	1.13	0.37	3.99
HEP	3.00	71.6 (9.7)	79.7 (4.6)	1.88	0.50	5.50
PHBA	3.95	59.4 (3.8)	75.4 (5.8)	2.62	0.66	4.80
BHA	3.42	93.3 (14)	81.8 (11)	2.09	0.57	7.12
BHT	13.7	90.2 (6.7)	58.7 (5.6)	11.6	2.28	33.0
BPA	0.63	101 (3.0)	94.7 (0.8)	0.33	0.11	1.17
DES	2.16	85.0 (4.3)	75.3 (1.5)	1.43	0.36	3.96
E1	0.44	103 (2.2)	83.7 (6.7)	0.26	0.07	0.81
E2	1.10	121 (7.2)	85.7 (8.3)	0.64	0.18	2.71
E3	1.78	118 (2.7)	85.0 (4.5)	1.05	0.30	3.44
EE2	2.80	100 (10)	84.6 (7.4)	1.66	0.47	7.30
OPP	0.89	102 (6.9)	97.6 (5.0)	0.46	0.15	1.52
TCS	0.42	101 (14)	88.3 (8.8)	0.24	0.07	1.03
TCC	0.89	99.4 (8.0)	83.1 (8.2)	0.54	0.15	2.36
4-*t*-OP	1.80	121 (9.4)	77.1 (4.2)	1.17	0.30	3.68
NP	0.75	125 (1.5)	73.6 (2.6)	0.51	0.13	1.61

a IDL: instrumental detection limit;

b: Relative R: Relative recoveries, recoveries relative the internal standards;

c: Absolute R: Absolute recoveries, the true recoveries during the SPE procedures;

d: MDL: method detection limit;

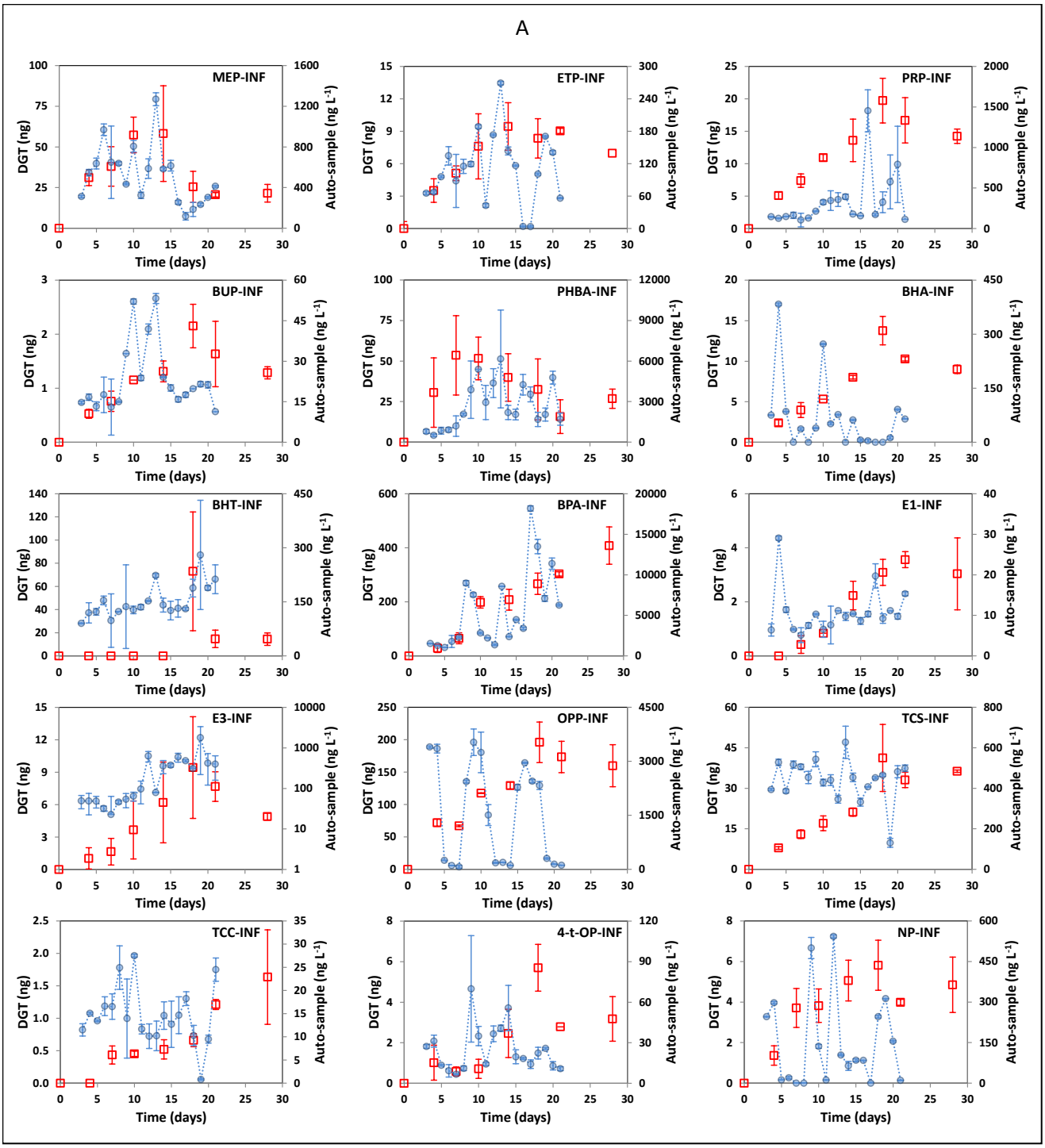
e: calculated using the equation: $\mathrm{MDL}=\frac{\mathrm{IDL}}{\mathrm{R}\times\mathrm{CF}}$,[2] where R is the absolute recovery and the CF is the concentration factor, which is 2000 for active sample in this study;

f: MDL for DGT samples were calculated based on the 7-day deployment in the field application under 25 ℃ condition.

Table S3: Diffusive coefficients (D_e, 10^{-6} cm^2 s^{-1}), some data on sampling rates (R_S, L d^{-1}) and R_S per unit ($R_{S/A}$, L $(d•cm^2)^{-1}$) for target compounds.

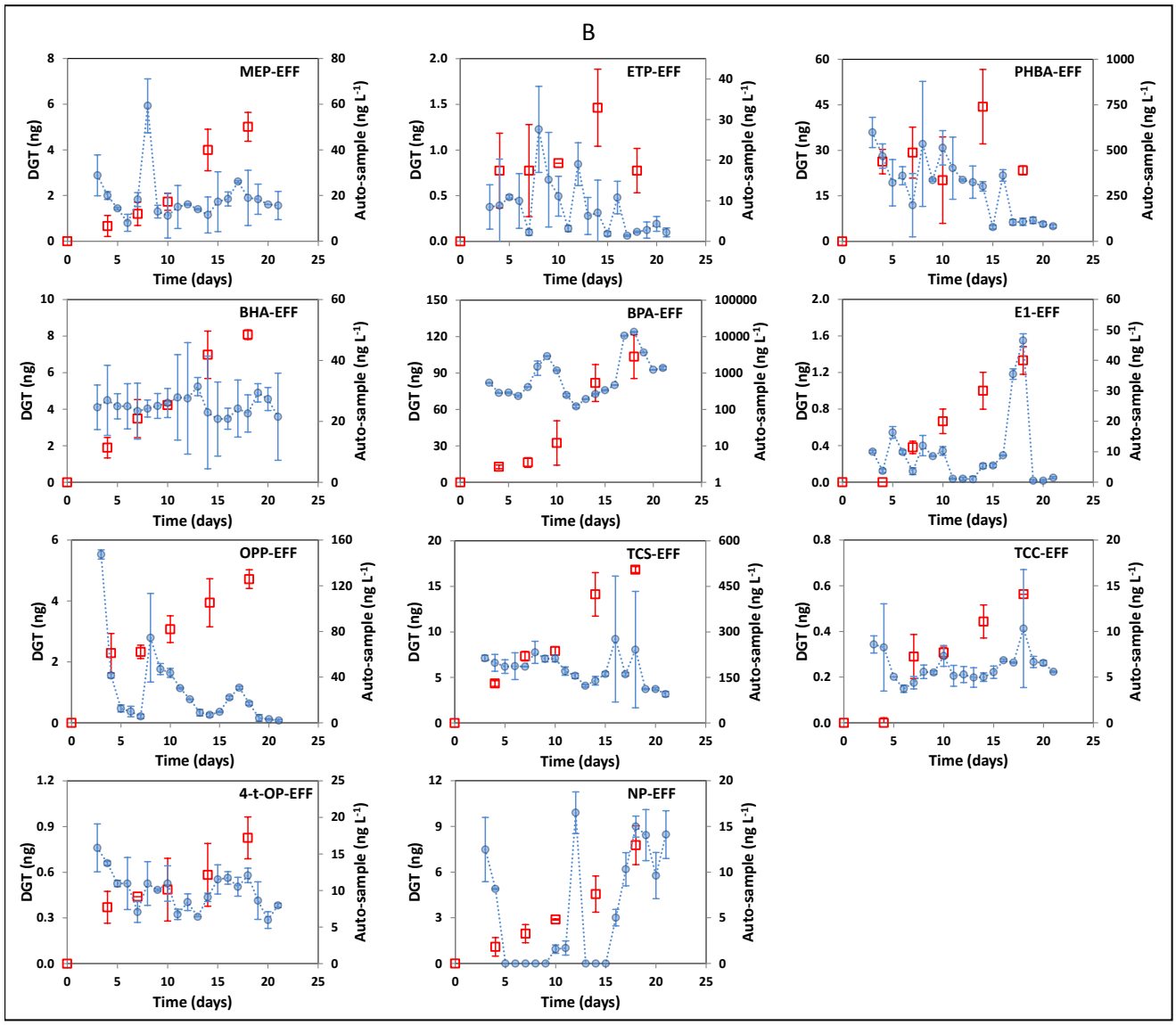
Sampler	Area/ cm^2	T/℃	Type	MEP	ETP	PRP	BUP	BEP	HEP	PHBA	BHA	BHT	OPP	TCS	TCC	BPA	DES	E1	E2	E3	EE2	4-T-OP	NP	Ref
DGT	3.14	25	D_e	6.85	6.45	5.92	5.61	4.97	4.83	7.30	4.25	3.67	5.18	3.63	3.36	4.80	4.83	4.80	3.58	4.59	3.40	4.34	4.13	This study
			R_S	0.019	0.018	0.016	0.015	0.013	0.013	0.020	0.012	0.010	0.014	0.010	0.009	0.013	0.013	0.013	0.010	0.012	0.009	0.012	0.011	This study
				-[a]	-	-	-	-	-	-	-	-	-	-	-	0.014	-	-	-	-	-	-	-	3
			$R_{S/A}$	5.92	5.58	5.12	4.85	4.29	4.18	6.31	3.68	3.17	4.47	3.14	2.90	4.15	4.18	4.15	3.09	3.97	2.94	3.75	3.57	This study
POCIS	45.8	25	R_S	-	-	-	-	-	-	-	-	-	-	-	-	0.088	-	0.129	0.114	0.131	0.214	0.110	0.105	4
			$R_{S/A}$	-	-	-	-	-	-	-	-	-	-	-	-	1.92	-	2.82	2.49	2.86	4.67	2.40	2.29	
			R_S	-	-	-	-	-	-	-	-	-	-	-	-	0.117	-	0.120	0.115	0.157	0.222	0.120	0.117	4
			$R_{S/A}$	-	-	-	-	-	-	-	-	-	-	-	-	2.55	-	2.62	2.51	3.43	4.85	2.62	2.55	
	45.8	20	R_S	-	-	-	-	-	-	-	-	-	-	-	-	0.245	-	0.230	0.221	0.185	0.260	0.065	-	5
			$R_{S/A}$	-	-	-	-	-	-	-	-	-	-	-	-	5.35	-	5.02	4.83	4.04	5.68	1.42		
	45.8	-	R_S	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.018	0.014	0.019	-	-	-	6
			$R_{S/A}$	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.39	0.31	0.41	-	-	-	
	45.8	28	R_S	-	-	-	-	-	-	-	-	-	-	1.920	-	-	-	-	-	-	-	-	-	7
			$R_{S/A}$	-	-	-	-	-	-	-	-	-	-	41.92	-	-	-	-	-	-	-	-	-	
	41	15	R_S	-	-	-	-	-	-	-	-	-	-	1.442	-	0.740	-	0.636	0.596	-	0.751	-	1.654	8
			$R_{S/A}$	-	-	-	-	-	-	-	-	-		35.17	-	18.05	-	15.51	14.54	-	18.32	-	40.34	
	41	25	R_S	-	-	-	-	-	-	-	-	-	-	1.060	-	0.607	-	0.793	0.702	-	-	-	-	9
			$R_{S/A}$	-	-	-	-	-	-	-	-	-	-	25.85	-	14.80	-	19.34	17.12	-	-	-	-	
	25.12	18	R_S	-	-	-	-	-	-	-	-	-	-	-	-	0.033	-	0.040	0.059	0.150	-	-	-	10
			$R_{S/A}$	-	-	-	-	-	-	-	-	-	-	-	-	1.31	-	1.59	2.35	5.97	-	-	-	
	17.1	-	R_S	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.058	-	11
			$R_{S/A}$	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	3.39	-	
	11.45	15	R_S	-	-	-	-	-	-	-	-	-	-	-	-	0.040	-	0.040	0.037	-	0.051	-	-	12
			$R_{S/A}$	-	-	-	-	-	-	-	-	-	-	-	-	3.49	-	3.49	3.23	-	4.45	-	-	
Chemcatcher	15.9	20	R_S	-	-	-	-	-	-	-	-	-	-	-	-	0.104	-	0.127	0.162	-	-	0.022	-	13
			$R_{S/A}$	-	-	-	-	-	-	-	-	-	-	-	-	6.54	-	7.99	10.19	-	-	1.38	-	

a -: no data available.


A
MEP-INF
ETP-INF
PRP-INF
BUP-INF
PHBA-INF
BHA-INF
BHT-INF
BPA-INF
E1-INF
E3-INF
OPP-INF
TCS-INF
TCC-INF
4-t-OP-INF
NP-INF
DGT (ng)
Auto-sample (ng L-1)
Time (days)

94
95

96



97
98

99 **Figure S1:** TOrCs uptake in DGT (ng, n=3, red dots) and average auto-sample concentrations (n = 2, ng

100 L^{-1}, blue line with round dots) for detected TOrCs in both influent (A) and effluent (B) in a WWTP. Error

101 bar: 1 sd.

102

103

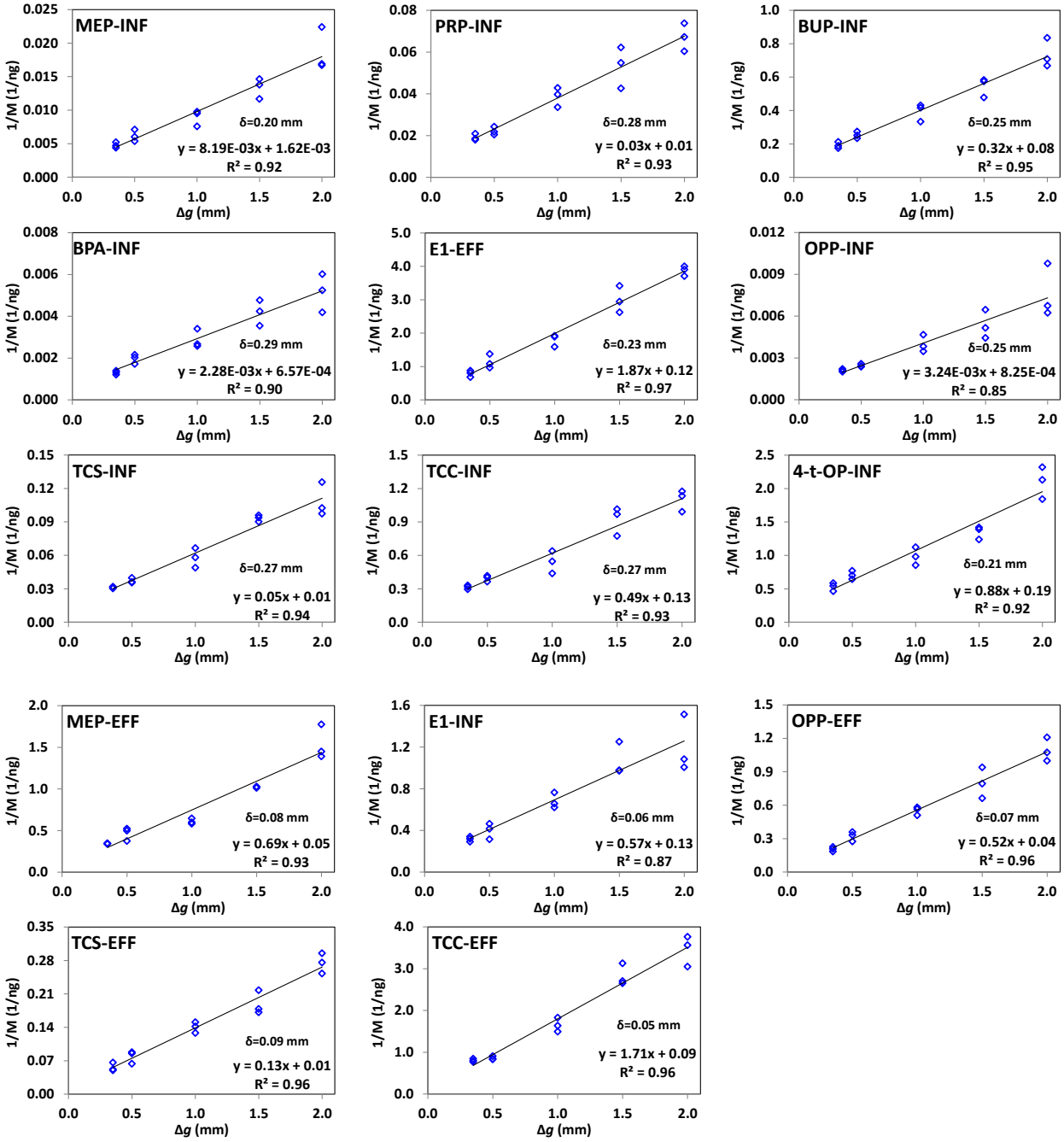


Figure S2: Plot of 1/mass (1/*M*, 1/ng) of TOrCs accumulated by DGT (n=3) deployed in both influent (INF) and effluent (EFF) versus different diffusive gel thickness (Δ*g*, mm).

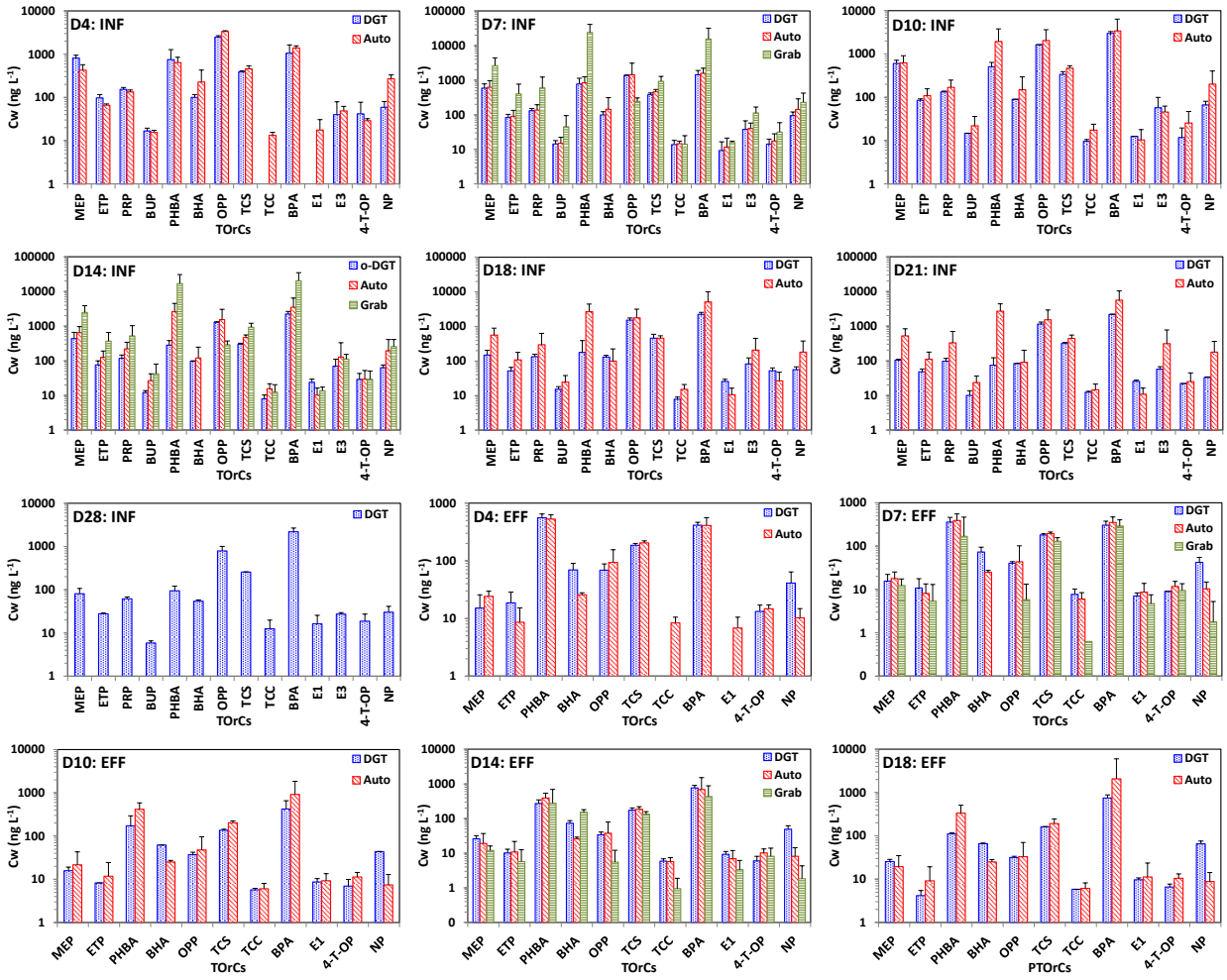
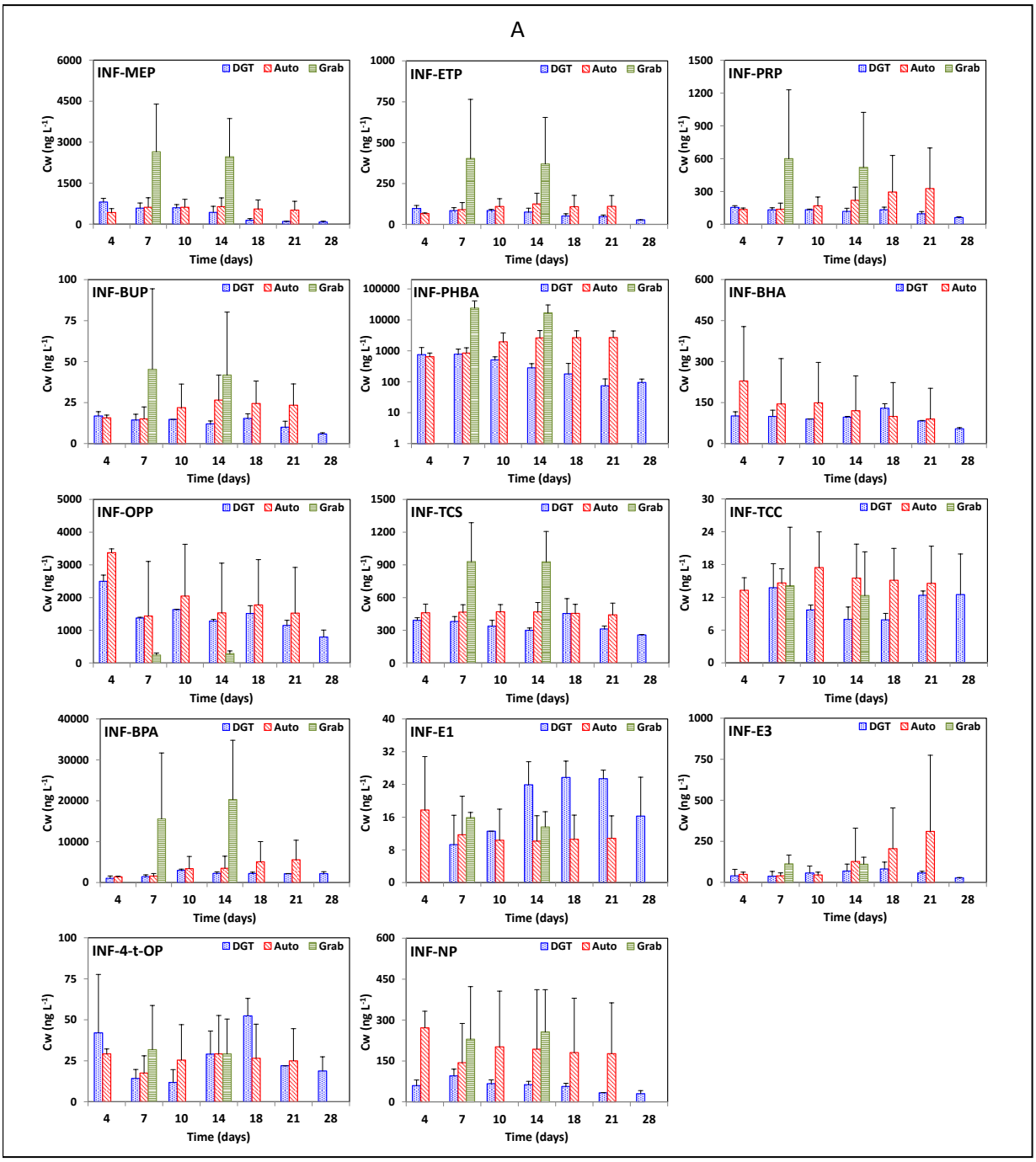


Figure S3: 4, 7, 10, 14, 18, 21 and 28-day average concentrations of DGT (n=3), auto and grab samples for compounds detected by DGT in influent and effluent, Error bar: 1 sd.


A
INF-MEP
INF-ETP
INF-PRP
INF-BUP
INF-PHBA
INF-BHA
INF-OPP
INF-TCS
INF-TCC
INF-BPA
INF-E1
INF-E3
INF-4-t-OP
INF-NP
DGT
Auto
Grab
Cw (ng L-1)
Time (days)

114
115
116

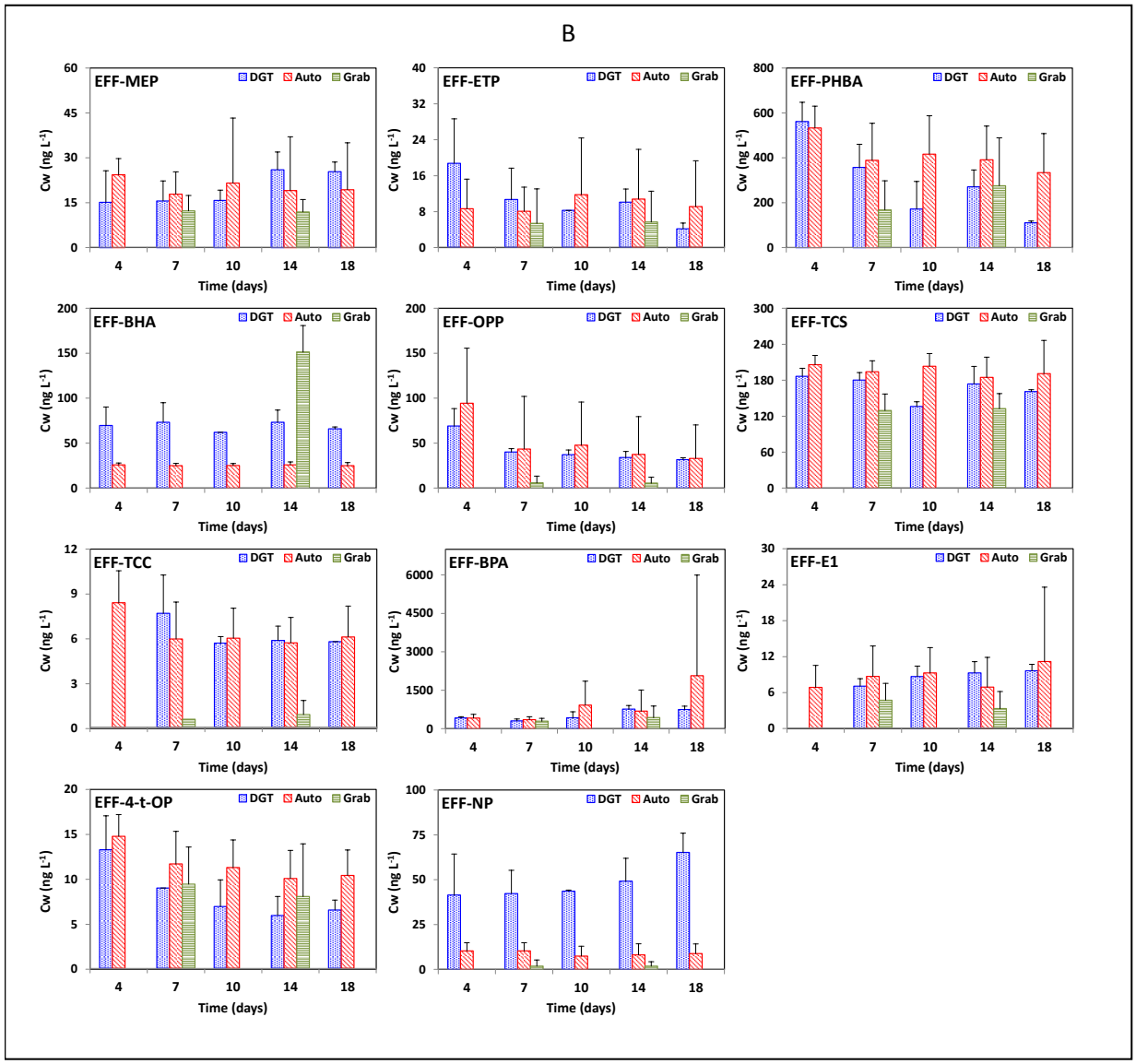
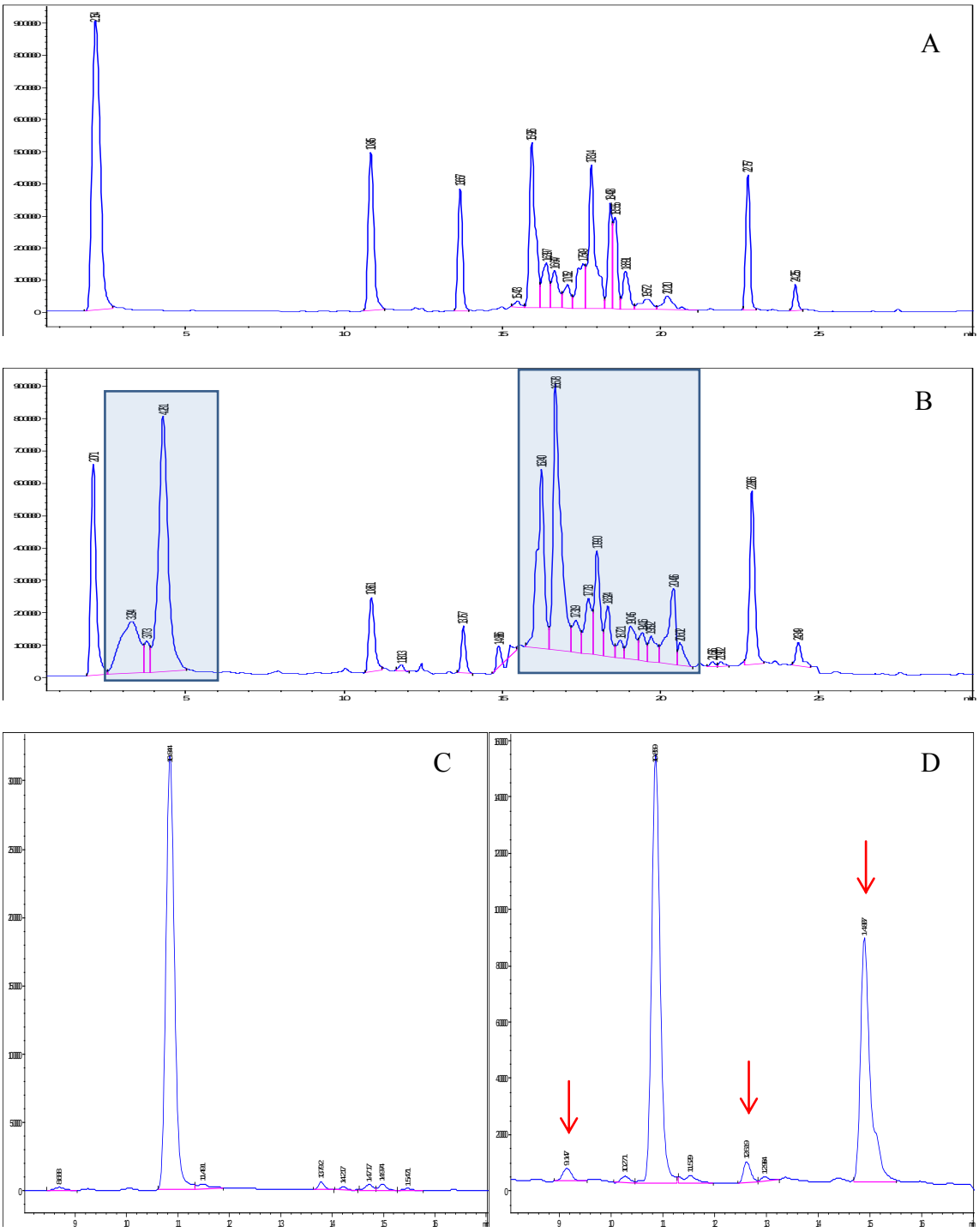


Figure S4: TWA concentrations of DGT (n = 3,), average concentrations of auto and grab samples for typical compounds in both influent (A) and effluent (B) for different days, Error bar: 1 sd.

122



123

124 **Figure S5:** Total ionic chromatograms and extracted ion chromatograms of MEP-151 for 14-day DGT

125 sample (A and C) and 14th day's auto sample (B and D) in the influent scanned by the SIM mode.

References

1. Chen, W.; Huang, H.; Chen, C.-E.; Qi, S.; Price, O. R.; Zhang, H.; Jones, K. C.; Sweetman, A. J., Simultaneous determination of 20 trace organic chemicals in waters by solid phase extraction (SPE) with triple-quadrupole MS (QqQ-MS) and hybrid quadrupole Orbitrap high resolution MS (Q-Orbitrap-HRMS). *Submitted* **2016**.
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Paper V

Fate of Trace Organic Chemicals at Chinese Wastewater Treatment Plants (WWTPs): Occurrence and Removal Based on DGT Techniques

Fate of Trace Organic Chemicals at Chinese Wastewater Treatment Plants (WWTPs): Occurrence and Removal Based on DGT Techniques

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16 **TOC**

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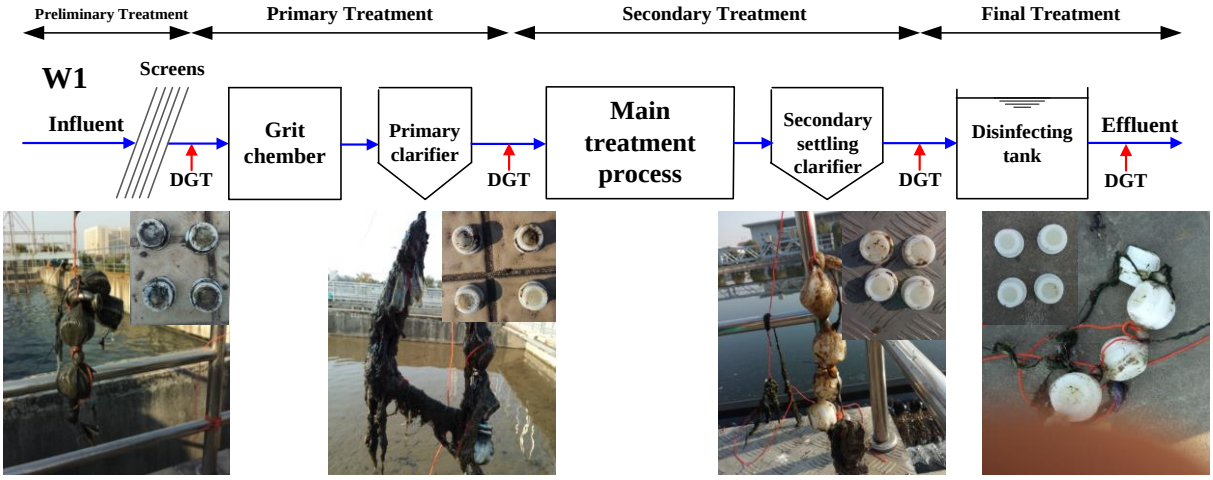

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ABSTRACT:

The occurrence of trace organic chemicals (TOrCs) in the aquatic environment has been of increasing concern due to their potential risk to humans and ecosystems. Diffusive gradients in thin-films (DGT) passive samplers were employed to study the fate of 20 TOrCs in 10 wastewater treatment plants (WWTPs) in Wuhan and Dalian, China. TOrCs in the raw influent, primary effluent, secondary effluent and final effluent were sampled by DGT with hydrophilic-lipophilic-balanced (HLB) resin as binding gel and analysed by liquid chromatography-tandem mass spectrometry (LC-MS/MS). TOrCs were widely detected in the wastewater (all in the raw influent and 18 in the final effluent), with 100% detection frequencies for methylparaben, propylparaben, 4-hydroxybenzoic acid, triclocarban and nonylphenol in the final effluent. No significant differences were observed in the raw influent for the majority of TOrCs between two cities and between urban and sub-urban areas. The removal for the majority of TOrCs was > 50 %. Loss during primary treatment and secondary (biological) treatment made the greater contributions to removal. Mass loading and emission analysis showed that WWTPs released a large amount of TOrCs via effluent wastewater discharge because of incomplete elimination of TOrCs.

1. INTRODUCTION

Preservatives, antioxidants, disinfectants, oestrogens and alkyl-phenols are groups of trace organic chemicals (TOrCs)[1], which are consumed for daily life in modern society. Due to their wide applications, continuous discharge after usage and the nature of these chemicals, the distribution and transport of these TOrCs are primarily associated with the aquatic environment.[2, 3] The effects of exposure to mixtures of TOrCs and their potential risks to human health and aquatic organisms are still largely unknown.[4, 5] Thus, fate and behaviour studies of TOrCs in the environment are needed.

Conventional wastewater treatment plants (WWTPs) are normally designed for removal of traditional pollutants (e.g. metals, nutrients and biodegradable organic matter) and undesirable fractions (e.g. solids and suspended particulates). There are no specifically-designed treatment units for elimination of TOrCs.[6-10] Residual TOrCs discharged in treated effluent wastewater may contribute to their ubiquitous detection in the aquatic environment.[11, 12] Studies have been conducted around the world on the occurrence and removal of TOrCs in WWTPs around the world,[7, 13-19] but few have considered the performance of different treatment processes/techniques on the elimination of TOrCs or assessed the effects of parameters (including the size, age and treatment processes) on removal efficiency.

The passive sampling technique of diffusive gradients in thin-films (DGT) offers the time-weighted average (TWA) concentrations of TOrCs in the aquatic environment.[20, 21] A recent study showed the potential of DGT to study the fate and behaviour of antibiotics in WWTPs.[22] It has many advantages over conventional grab or auto sampling methods, although the results of most field research until now are relied on conventional methods, which are cost- /time-

consuming and may not reflect integrated picture of TOrCs levels/discharge for the monitoring programs. More recently, a new DGT passive sampling device, using hydrophilic-lipophilic-balanced (HLB) resin as the binding agent, was developed for TOrCs[23, 24] and tested in a WWTP,[25] providing comparable results with auto-sampler.[25] Thus, in this present study the DGT passive sampling technique was utilised to: 1) study the occurrences and levels of TOrCs in a large scale campaign of 10 Chinese WWTPs, 2) determine the removal efficiency of these chemicals among and within the WWTPs, 3) assess the effects of parameters (including the size, age and treatment processes) on the removal efficiency for WWTPs and 4) estimate the mass loading and emission of TOrCs from the WWTPs.

2. MATERIALS AND METHODS

2.1 Chemical and Reagents

Twenty high purity standards of TOrCs, including methylparaben (MEP), ethylparaben (ETP), propylparaben (PRP), butylparaben (BUP), benzylparaben (BEP) and heptyl paraben (HEP), 4-hydroxybenzoic acid (PHBA), butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), ortho-phenylphenol (OPP), triclosan (TCS), triclocarban (TCC), bisphenol-A (BPA), diethylstilbestrol (DES), estrone (E1), β-estradiol (E2), estriol (E3), 17α-ethinylestradiol (EE2), 4-*tert*-octylphenol(4-*t*-OP) and nonylphenol (NP) were purchased from Sigma-Aldrich (UK). The structures and the physicochemical properties of chemicals were listed in supporting information (SI) **Table S1**.

Isotope-labelled internal standards (ISs), including ^{13}C MEP, ^{13}C BUP, ^{13}C PRP, ^{13}C BUP, BHA-d_3, ^{13}C OPP and BPA-d_{16} were purchased from Sigma-Aldrich (UK), other ISs including PHBA-d_4, BHT-d_{24}, TCS-d_3, E1-d_4, E2-d_5, E3-d_2, EE2-d_4, 4-n-OP-d_{17} and 4-n-NP-d_4 were purchased

from QMX Laboratories (UK). The standard solutions for the target chemicals and ISs were prepared according to a previous study.[26]

Organic solvents, including methanol (MeOH) and acetonitrile (ACN) are HPLC-grade, which are obtained from Fisher Scientific (UK). Reagents are at least analytical grade with ≥ 99 % purity, ammonia solution (NH_4OH, 5 M) was purchased from Sigma-Aldrich (UK). Pure water used in the study was supplied from a Milli-Q water (MQ water) purification system (> 18.2 MΩ/cm, Millipore, UK).

2.2 WWTP Descriptions and DGT Deployment

With the rapid development of industralisation and urbanisation, the consumption of the water resources is increasing significantly in China leading the great expansion in the wastewater treatment industry in last two decades, especially since 2000. According to the data from Ministry of Environmental Protection of China, 4436 WWTPs have been built by the end of 2014, more than 30 times the numbers in 1995. The total capacity of wastewater treatment reached more than 171 million m^3/d in 2015, about 23 times larger than in 1995. Among all the built WWTPs, activated sludge (AS) based techniques are most widely-used main (secondary) processes in China, which sequencing batch reactor (SBR), oxidation ditch (OD), anaerobic/oxic (A/O) and anaerobic/anoxic/oxic (A2/O) processes, the biological aeration filter (BAF) process which belongs to another important process-biofilm-process, was also selected.[27] To widely study the occurrences of TOrCs in these WWTPs and assess if these WWTPs are efficient in removing TOrCs, 10 typical full-scale municipal WWTPs covering these 5 processes were selected in 2 different cities (Wuhan and Dalian, 5 WWTPs in each city) of China for this study. Summary information on the WWTPs is given in **Table 1**, and a schematic diagram of each WWTP is given in **Figure S1**.

Table 1: Summary of 10 selected WWTPs for DGT deployment.

WWTP number	Starting year	Main process	Urban/sub-urban	Designed capacity /10^4 m^3 per day	Average flow /10^4 m^3 per day	Service people /10^3 people
W1	2007	A/O	Urban	30	28.96	940
W2	2013	SBR	Sub-urban	2	1.1	70
W3	1993	A2/O	Urban	15	14.78	300
W4	2006	OD	Sub-urban	5	5.21	110
W5	2008	OD	Sub-urban	10	7.76	460
D1	2011	A2/O	Urban	10	8.91	320
D2	2001	A/O	Sub-urban	1	0.84	50
D3	2012	SBR	Sub-urban	1	0.85	50
D4	2008	BAF	Urban	8	7.28	600
D5	1986	BAF	Urban	12	11.74	350

In each WWTP, pre-prepared standard DGT samplers with HLB resin as the binding gel and agarose (1 mm) as diffusive layer[23] were deployed 30 cm below the water surface at four sites, to sample the from raw influent (RI), primary effluent (PE), and secondary effluent (SE) to final effluent (FE), see **Figure S1**.The water temperature at these four sites during the sampling period is in the range of 13.4-18.7 ℃, 12.2-18.6 ℃, 13.6-18.4 ℃ and 12.3-18.7℃, respectively. DGT devices were deployed in triplicate at each site for 7 days as recommended from a previous study.[25] Water temperature and pH were recorded during DGT deployment and retrieval. Field bank DGT samplers were also prepared.

2.3 Sample Extraction and Analysis

DGT samplers were retrieved after 1 week deployment, and the binding gels of each sampler were then taken out and extracted following the method established in the previous study.[25] In brief, the resin gel was placed in a pre-cleaned and baked amber sample vial and 5 mL ACN and 100 ng of ISs were added. The vials were then placed into an ultrasonic bath for 30 minutes extraction. The extracts were blown down to about 1 mL under a gentle flow of N_2 and syringe

filtered (0.22 μm, PTFE, Whatman) into amber vials. Just before the instrumental analysis, 300 μL aliquot of DGT samples were dried under a gentle N_2 flow and reconstituted in 50 μL of water and methanol mixture with 5 mM NH_4OH (50 % : 50 %, v/v). A liquid chromatography-tandem mass spectrometry (LC-MS/MS, Waters, UK) was used to determine and quantify the TOrCs in the DGT samples using the multiple reaction monitoring (MRM) mode.[26] Details of the instrumental analysis and the method detection limits (MDLs) are given in **SI**.

Quality assurance and quality control (QA/QC) procedures were conducted throughout from field sampling to instrumental analysis. Sample replicates, field blanks, procedural blanks and instrumental blank samples were all analysed.

2.4 Concentration and Removal Calculation

The TWA concentrations of TOrCs in the water (C_W) measured by DGT were calculated using Equation (1):[21]

$$C_W = \frac{M\Delta g}{D_e A t} \quad (1)$$

where M is the measured mass of TOrC accumulated in the binding gel, Δg is the thickness of the diffusive layer, D_e is the diffusion coefficient of target TOrC measured previously,[25] t is the exposure time and A is the exposure window area.

The overall performance for the WWTPs was evaluated by the overall removal efficiency (R_O, %) of TOrCs. Contribution of each treatment process/technique within a single WWTP could also be assessed as the relative removal efficiency for each treatment unit (R_R, %). They were be calculated using Equations (2) and (3):[28]

$$R_{\mathrm{O}} = \frac{c_{\mathrm{INF}} - C_{\mathrm{EFF}}}{C_{\mathrm{INF}}} \times 100\% \quad (2)$$

$$R_{\mathrm{R}\text{-}i} = \frac{c_{\mathrm{IN}\text{-}i} - C_{\mathrm{OUT}\text{-}i}}{C_{\mathrm{INF}}} \times 100\% \quad (3)$$

where the C_{INF} (ng/L) and C_{EFF} (ng/L) is the chemical concentration in raw influent and final effluent, $C_{\mathrm{IN}\text{-}i}$ (ng/L) and $C_{\mathrm{OUT}\text{-}i}$ (ng/L) is the chemical concentration in inflow and outflow of each treatment unit i (primary, secondary or disinfection). The sum of R_{R} for treatment steps is R_{O}.

The mass loadings (M, μg/d) of the aqueous TOrCs in the raw influent and the emissions or discharges (E, μg/d) of aqueous TOrCs in the final effluent were estimated using Equations (4) and (5):[9, 28]

$$M = C_{\mathrm{INF}} \times Q \quad (4)$$

$$E = C_{\mathrm{EFF}} \times Q \quad (5)$$

where Q (m^3/d) is the wastewater treatment flow for the WWTP per day.

Statistical analysis was conducted using IBM *SPSS* Statistics software (Version 22). Concentrations of TOrCs below the MDLs were assigned as half of the MDLs for descriptive data statistics, and assigned as zero for removal efficiency calculations. The average of the three triplicate samples at each site was used to calculate the removal efficiency and for analysis of variance (ANOVA) test. Significant differences were tested by ANOVA at the 5 % significance level.

3. RESULTS AND DISCUSSION

3.1 Occurrence of TOrCs in WWTPs

The range, mean and median concentrations and the detection frequency of 20 target TOrCs in the raw influent, primary effluent, secondary effluent and final effluent are shown in **Table S2**. The average concentrations of individual TOrCs in the raw influent, primary effluent, secondary effluent and final effluent ranged from < MDL to 1795 ng/L, < MDL to 1268 ng/L, < MDL to 578 ng/L and < MDL to 586 ng/L, respectively. As we could notice that the average concentrations (**Figure 1**) of the TOrCs in wastewater show great differences among the WWTPs, this could be resulted from the different application of the TOrCs and their emissions in various service areas, the patterns (different between urban and sub-urban areas) of the application of the products which contain these TOrCs.

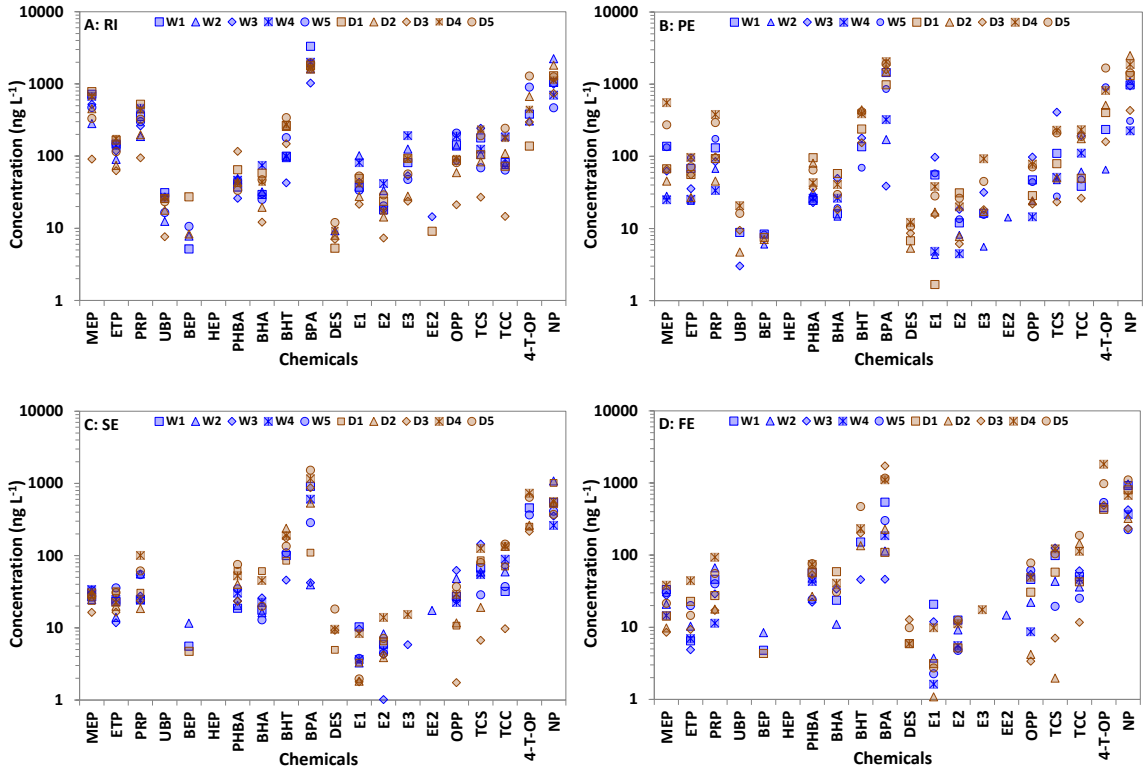


Figure 1: Mean of TOrC concentrations in raw influent (RI, A), primary effluent (PE, B), secondary effluent (SE, C) and final effluent (FE, D) in 10 WWTPs (n=30).

The average concentrations of ∑TOrCs (sum of 20 individual TOrC) in the raw influent, primary effluent, secondary effluent and final effluent were 5185 ± 1107, 3856 ± 1971, 1911 ±734 and 1820 ±1028 ng/L, respectively. The average proportions of ∑preservatives (six parabens and PHBA), ∑antioxidants (BHA and BHT), ∑disinfectants (OPP, TCS and TCC), BPA, ∑oestrogens (DES, E1, E2, E3 and EE2) and ∑alkyl-phenols (4-*t*-OP and NP) in the raw influent, primary effluent, secondary effluent and final effluent are in **Figure 2**. It is obviously noticed that alkyl-phenols and BPA are the predominant TOrCs in the wastewater, accounting for > 60 % totally in the wastewater collected at all 4 sites of WWTPs. This showed that the wide application of the compounds in the daily products from these two regions, since alkyl-phenols widely exist in the detergents and BPA are applied in the plastic materials.

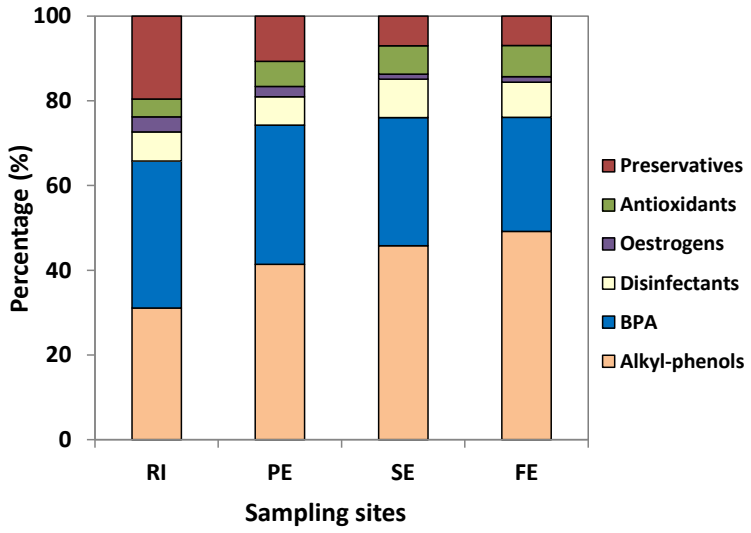


Figure 2: Percentage of TOrCs in raw influent (RI), primary effluent (PE), secondary effluent (SE,) and final effluent (FE) of 10 WWTPs (n=30).

Among 20 analysed TOrCs, all of them could be detected in influent and primary effluent from at least one of the 10 WWTPs, 19 (all except HEP) and 18 (all except BUP and HEP) were found

192 in secondary effluent and final effluent from at least one of the 10 WWTPs. In the raw influent,
193 15 TOrCs could be found in all of the samples with average concentrations ranging from 21.5
194 (BUP) to 1795 (BPA) ng/L. Among these 15 TOrCs, the highest average concentration was
195 observed for BPA, followed by NP (1165 ng/L) and MEP (499 ng/L). In the primary effluent, 12
196 TOrCs were detected in all the samples with average concentrations ranging from 26.7 (E1) to
197 1268 (BPA) ng/L. Among these 12 TOrCs, the highest concentration was observed for BPA,
198 followed by NP (1092 ng/L) and MEP (148 ng/L). In the secondary effluent, 10 TOrCs were
199 detected in all the samples with average concentrations ranging from 4.77 (E1) to 578 (BPA)
200 ng/L. Among these 10 TOrCs, the highest concentration was observed for BPA (578 ng/L),
201 followed by NP (568 ng/L) and TCC (78.1 ng/L). In the final effluent, only 5 of TOrCs were
202 detected in all the samples with average concentrations ranging from 21.6 (MEP) to 586 (NP)
203 ng/L. Among these 5 TOrCs, the highest concentration was observed for NP, followed by TCC
204 (67.7 ng/L) and PHBA (47.2 ng/L).

205 ## 3.2 Spatial Variation of TOrCs in WWTPs

206 Spatial variation analysis of TOrCs was conducted for the raw influent and final effluent of the
207 WWTPs between two different cities, and between urban and sub-urban/rural areas.

208 The average concentrations of detected TOrCs (**Table S3**) in raw influent and final effluent from
209 two different cities ranged from 3.62 ± 1.48 to 1863 ± 898 ng/L (Wuhan, n=15) and 2.73 ± 1.62
210 to 1731 ± 298 ng/L (Dalian, n=15), and < MDL to 580 ± 329 ng/L (Wuhan, n=15) and < MDL to
211 711 ± 496 ng/L (Dalian, n=15), respectively. No significant differences ($p > 0.05$) were observed
212 for the majority (13 in 20) of TOrCs in the raw influent of the WWTPs from two cities, while
213 significantly higher ($p < 0.05$) concentrations of E1, E2, E3 and OPP were detected in the raw
214 influent of WWTPs from Wuhan than from Dalian, and significantly lower ($p < 0.05$)

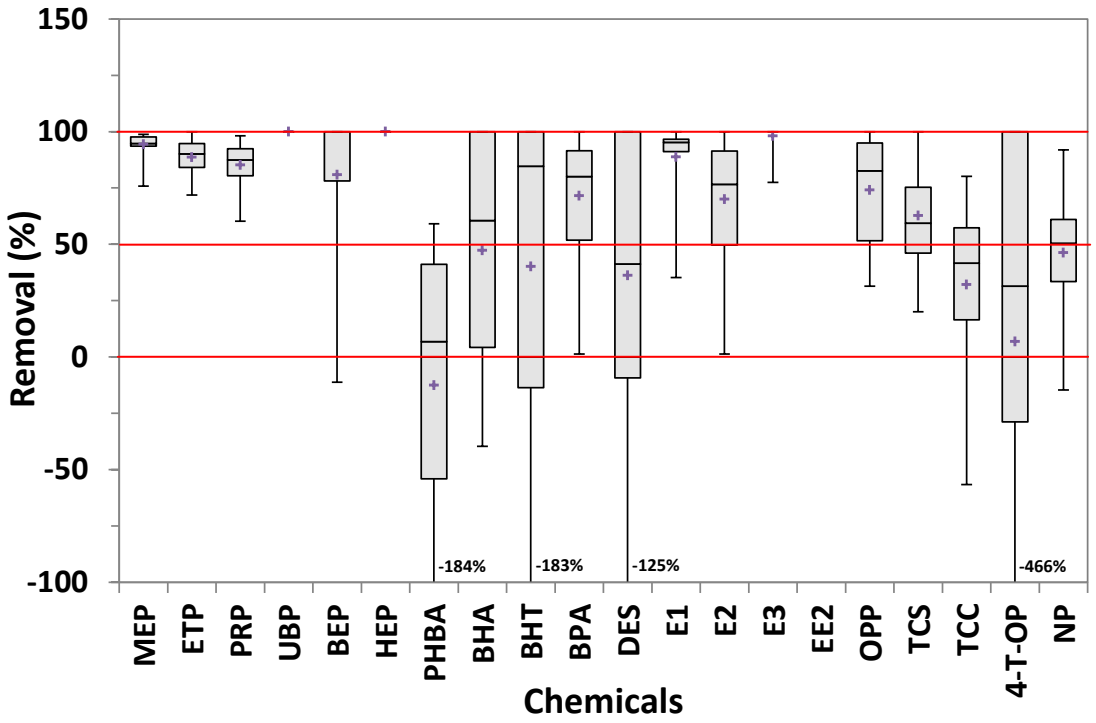
concentrations of PHBA, BHT and DES were found in Wuhan than in Dalian. In the final effluent, no significant differences ($p > 0.05$) were observed for 10 of 18 TOrCs in the final effluent among the WWTPs from two cities, while significantly higher ($p < 0.05$) concentrations of ETP, PHBA, BHT, BPA, DES, TCC and 4-*t*-OP were detected in the final effluent of WWTPs from Dalian than from Wuhan, and significantly lower ($p < 0.05$) concentrations of E1 were found in Dalian than in Wuhan. These results indicated the consumption of these TOrCs is similar in both cities.

The consumption of the TOrCs may vary with the urbanisation levels because of the different habits between urban and sub-urban/rural areas.[28] No significant differences ($p > 0.05$) were observed for the 11 of 20 TOrCs in the raw influent of the WWTPs between urban and sub-urban areas, while significantly higher ($p < 0.05$) concentrations of MEP, ETP, PRP, BUP, HEP BHA, EE2, and TCS were detected in the final effluent of WWTPs from urban areas than from sub-urban areas, and significantly lower ($p < 0.05$) concentration of PHBA were found in urban areas than in sub-urban areas. In the final effluent, significant differences ($p < 0.05$) were observed for the majority of detected TOrCs (12 of 18, see **Table S4**) in the final effluent of the WWTPs between urban and sub-urban areas. For all these 12 TOrCs, significantly higher concentrations were found in the urban area than in the sub-urban area.

3.3 Removal of TOrCs in WWTPs

The overall removal efficiency (R_O, %) was calculated to evaluate the removal of TOrCs from the WWTPs. The R_O for 19 TOrCs (except EE2) from 10 WWTPs, which were detected from more than half of the raw influent samples, were calculated and showed in **Figure 3** (R_O for individual WWTP was listed in **Table S5**). Very good overall removal was observed for parabens, for which the average R_O ranged from 81-100 %. Good removal was also observed for

238 oestrogens (except DES), BPA, OPP and TCS, with averages for the R_O > 50 %. The average R_O
239 for the alkyl-phenols, antioxidants, DES and TCC were < 50 %. The inefficiencies in alkyl-
240 phenol elimination from the WWTPs could be resulted from the application of materials in the
241 WWTPs which contains these chemicals. The average removal of PHBA in 10 WWTPs was < 0
242 %, which means production of the PHBA during the treatment process. This could be possible as
243 the PHBA is a metabolite of parabens degradation.[29, 30]



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245 **Figure 3:** Removal efficiencies of TOrCs in 10 WWTPs (n=30).

246 No significant differences (p > 0.05) in overall removal efficiencies were observed for the
247 majority (13 of 17) of TOrCs in the WWTPs between Wuhan and Dalian (**Figure 4**), while
248 significant differences (p < 0.05) in overall removal efficiencies were observed for 9 of 17
249 TOrCs in the WWTPs between urban and sub-urban areas. When looking at the average removal
250 of two cities, it seems the WWTPs in Wuhan have better removal for the major of the TOrCs

than in Dalian (more WWTP in Dalian have lower removals). And W4 (OD process) and W1 (A/O) in Wuhan have the best and worst removal among the WWTP in Wuhan, respectively. D2 (A/O) has the best removal in Dalian, and D4 (D5, BAF) has the worst removal in Dalian. It showed that the removal efficiencies of TOrCs could greatly change even for the same treatment process (A/O for example).

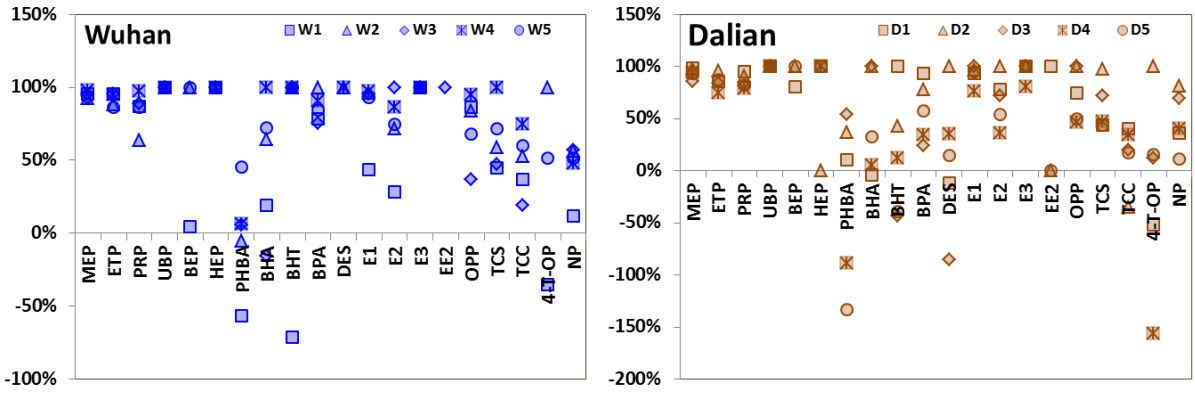

Figure 4: Average of overall removal for each WWTP is different Wuhan and Dalian.

The contribution of each treatment process/technique for the overall removal within a single WWTP was assessed by the relative removal efficiency for each treatment step. The relative removal efficiencies (R_R) of TOrCs for the different treatment steps in the 10 WWTPs are given in **Figure 5**. The average R_R of individual TOrCs for primary, secondary and final treatment in 10 WWTPs ranged from -57 to 100 %, 23 to 141 %, and -23 to 133 %, respectively. The primary and secondary treatment units contributed to the most removal of the TOrCs. Especially for antioxidants and alkyl-phenols, the secondary treatment is the key process to remove these compounds. The final treatment of disinfection as well as the microfiltration, sand filter and etc. is ineffective on the removal of the TOrCs.

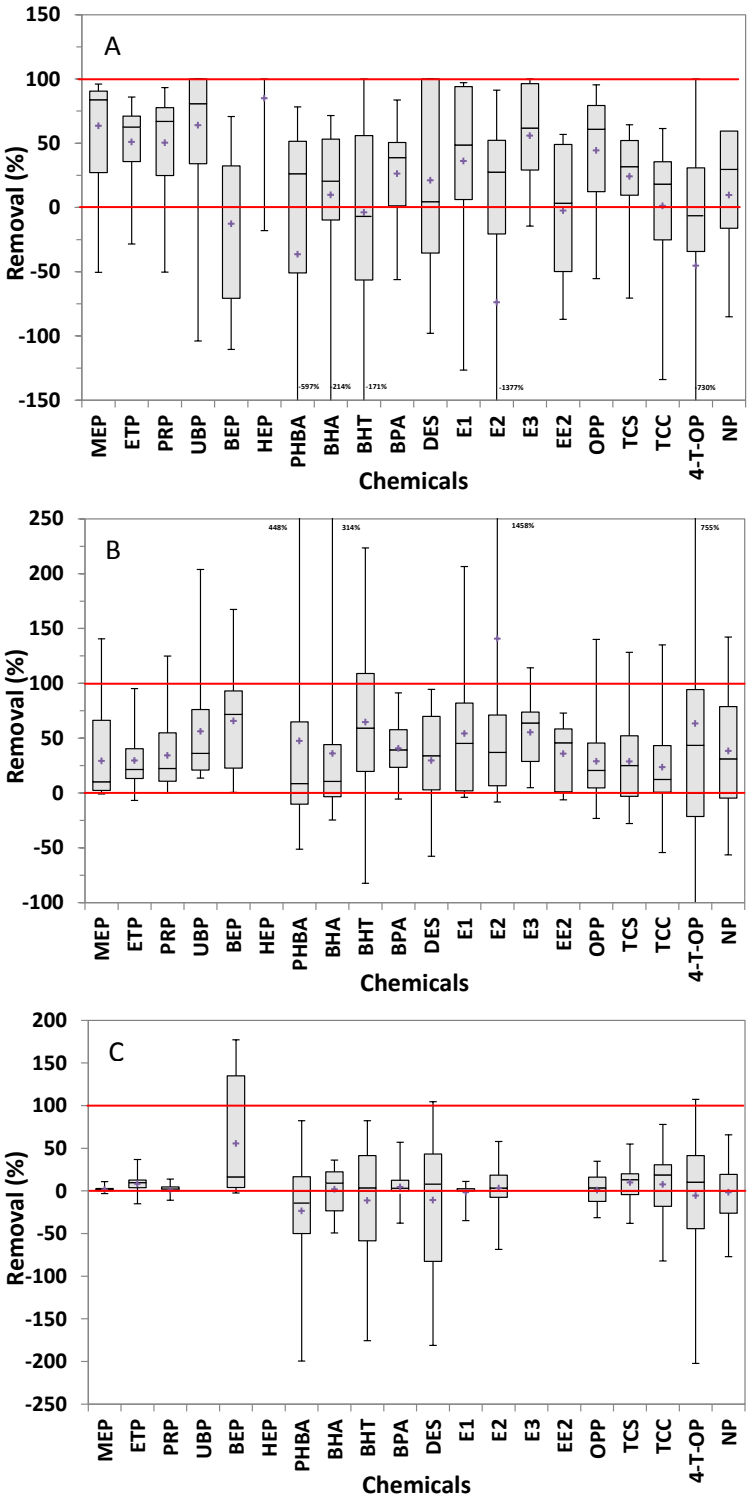

Figure 5: Relative removal efficiencies of TOrCs for primary treatment (A), secondary treatment (B) and final treatment (C) in 10 WWTPs (n=30).

3.4 Mass Loading and Emission of TOrCs

WWTP is one of the major sources of TOrCs emissions into the environment via effluent wastewater discharge with incompletely-eliminated TOrCs.[12, 13] The average mass loadings of the aqueous TOrCs in the raw influent and the aqueous TOrCs emissions from the final effluent of the 10 WWTPs were listed in **Table 2**. The average mass loadings and emissions of total aqueous TOrCs from the 10 selected WWTPs ranged from 28.1 to 1943 g/d and 8.62 to 779 g/d, respectively. The mass loading from the influent and emissions from the effluent of aqueous TOrCs per inhabitant could be estimated based on the service population for each WWTP, and the average results listed in the **Table S6**. The average mass loadings and emissions of total aqueous TOrCs per inhabitant for the people served by the 10 selected WWTPs ranged from 562 to 2388 μg/d per inhabitant and 172 to 1329 μg/d per inhabitant, respectively.

No significant differences ($p > 0.05$) of mass loadings were observed for the majority (15 of 20) of the chemicals between Wuhan and Dalian (**Table S7**), which is similar with the spatial variation results of TOrC concentrations in the raw influents. Significant larger ($p < 0.05$) of mass loadings were found for the TOrCs in urban area than in sub-urban area, indicating that consumption of these TOrCs varies with the urbanisation levels. Very similar results of aqueous TOrCs emissions with the mass loadings were observed between Wuhan and Dalian, and between urban area and sub-urban area.

Table 2: Average mass loadings and emissions of TOrCs in 10 WWTPs (g/d).

		W1	W2	W3	W4	W5	D1	D2	D3	D4A	D5
Mass Loadings	Preservatives	376	6.88	141	70.5	77.0	142	6.66	3.17	98.6	97.8
	Antioxidants	37.4	1.39	12.7	9.03	15.9	28.8	2.32	1.36	23.1	45.5
	Oestrogens	40.5	2.99	55.42	16.7	8.18	15.9	0.67	0.55	11.8	17.9
	Disinfectants	116	3.51	60.1	25.9	26.4	23.5	2.11	0.53	36.8	60.5
	BPA	960	11.8	151	104	148	158	13.5	13.7	124	230

	Alkyl-phenols	413	27.9	146	36.5	106	131	20.9	8.79	114	298
	Total TOrCs	1943	54.5	567	263	381	499	46.2	28.1	408	750
Emission	Preservatives	43.4	1.64	12.1	4.12	9.12	11.4	0.51	0.80	18.4	20.1
	Antioxidants	50.7	0.24	6.66	0.71	1.40	6.23	1.15	1.73	19.9	58.8
	Oestrogens	11.3	0.34	2.74	0.70	0.98	1.62	0.06	0.17	3.40	3.40
	Disinfectants	48.5	1.12	35.5	2.89	8.22	11.0	1.24	0.16	20.6	39.0
	BPA	211	0.01	29.7	9.66	23.4	9.89	2.94	10.1	80.3	99.1
	Alkyl-phenols	414	10.7	63.2	19.0	50.6	110	2.71	4.11	100	245
	Total TOrCs	779	14.0	150	37.1	93.7	150	8.62	17.1	243	465

CONCLUSION

DGT devices were successfully employed to study the fate of TOrCs in 10 Chinese domestic WWTPs from Dalian and Wuhan of China. All of the chemicals can be detected in the raw influent and 90 % of them can be still detected after treatment, in the final effluent. The high detection frequency shows the wide application of these TOrCs in daily life products, they may pose adverse effect on human health and aquatic ecosystem. No significant differences of concentrations were observed in the raw influent for the majority of TOrCs between two cities and between urban and sub-urban areas, while the significant larger of mass loadings were found for the TOrCs in the urban area than in the sub-urban area, which could be resulted from the different urbanisation levels between urban and sub-urban areas. Loss of TOrCs during the primary treatment and secondary (biological) treatment made the greater contributions to removal of these compounds, but the new treatment processes or WWTPs may need to be pre-assessed before operation to make sure they can effectively remove the TOrCs, since the great variable removal efficiencies were found among the current WWTPs. This study demonstrated that DGT sampler is an effective tool to study the fate of TOrCs and their removal in the WWTPs, showing great advantages over traditional sampling methods.

ASSOCIATED CONTENT

Supporting Information

Information of the target TOrCs and detection limits for LC-MS/MS, schematic diagrams and DGT deployment sites for WWTPs. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declared no competing financial interest.

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Supporting information for

Fate of Trace Organic Chemicals at Chinese Wastewater Treatment Plants (WWTPs): Occurrence and Removal Based on DGT Techniques

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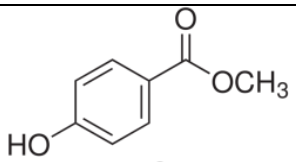
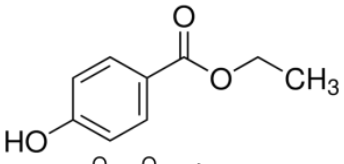
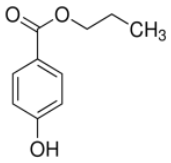
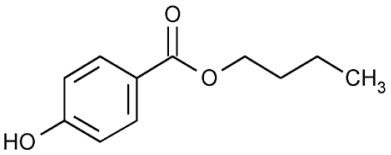
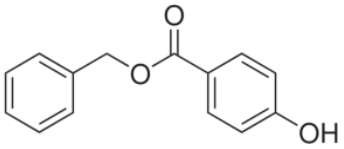
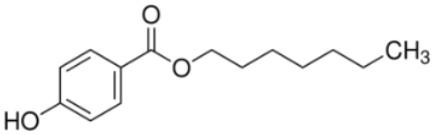
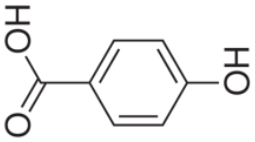
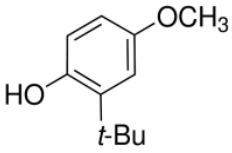
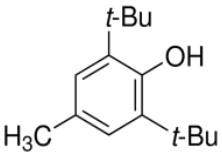
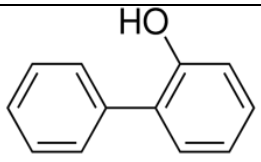
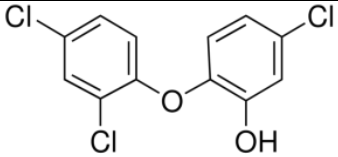
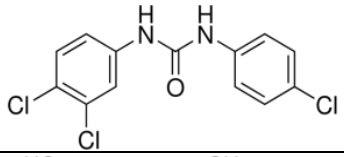
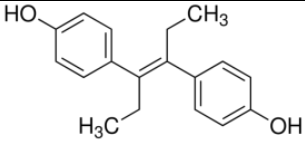
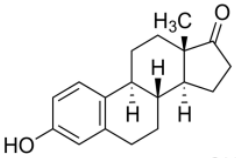
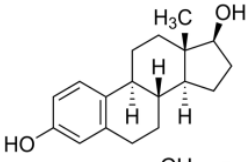
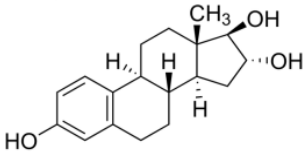
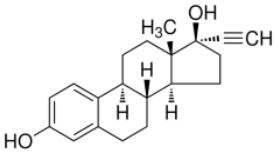
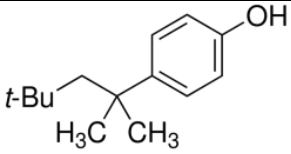
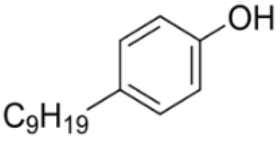
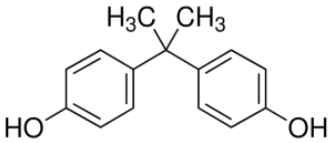
Table S1: Properties of TOrCs and their instrument detection limits (IDL, ng/L) and method detection limits (MDL, ng/L)[1].

Group	Chemical (Abbr.), CAS number and purity	Molecular formula and weight	Water solubility (mg L^{-1})	Structure	IDL	MDL for DGT samples[a]
Preservative	Methylparaben (MEP) 99-76-3 ≥ 99.0%	$C_8H_8O_3$ 152.15	2500		0.81	1.23
	Ethylparaben (ETP) 120-47-8 ≥ 99.0%	$C_9H_{10}O_3$ 166.17	885		1.43	2.31
	Propylparaben (PRP) 94-13-3 ≥ 99.0%	$C_{10}H_{12}O_3$ 180.2	500		1.18	2.07
	Butylparaben (BUP) 94-26-8 ≥ 99.0%	$C_{11}H_{14}O_3$ 194.23	207		1.27	2.35
	Benzylparaben (BEP) 94-18-8 ≥ 99.0%	$C_{14}H_{12}O_3$ 228.25	23.419		1.36	2.85
	Heptyl paraben (HEP) 1085-12-7 ≥ 99.0%	$C_{14}H_{20}O_3$ 236.31	8.022		1.44	3.10
	4-Hydroxybenzoic acid (PHBA) 99-96-7 ≥ 99.0%	$C_7H_6O_3$ 138.12	5000		3.18	4.53
Antioxidant	Butylated hydroxyanisole (BHA) 25013-16-5 ≥ 98.0%	$C_{11}H_{16}O_2$ 180.24	212.8		2.51	6.14
	Butylated hydroxytoluene (BHT) 128-37-0 ≥ 99.0%	$C_{15}H_{24}O$ 220.35	0.6		10.61	30.05
Disinfectant	Ortho-phenylphenol (OPP) 90-43-7 ≥ 99.0%	$C_{12}H_{10}O$ 170.21	700		0.86	1.33

[1] This table is continued onto the next page.

Group	Chemical (Abbr.), CAS number and purity	Molecular formula and weight	Water solubility (mg L^{-1})	Structure	IDL	MDL for DGT samples[a]
	Triclosan (TCS) 3380-34-5 ≥ 97.0%	$C_{12}H_7Cl_3O_2$ 289.55	10		0.40	4.20
	Triclocarban (TCC) 101-20-2 ≥ 99.0%	$C_{13}H_9Cl_3N_2O$ 315.59	0.65		0.83	0.88
Estrogen	Diethylstilbestrol (DES) 56-53-1 ≥ 99.0%	$C_{18}H_{20}O_2$ 268.36	12		1.96	4.15
	Estrone (E1) 53-16-7 ≥ 99.0%	$C_{18}H_{22}O_2$ 270.37	30		0.40	6.56
	β-estradiol (E2) 50-28-2 ≥ 98.0%	$C_{18}H_{24}O_2$ 272.39	3.9		0.96	1.72
	Estriol (E3) 50-27-1 ≥ 97.0%	$C_{18}H_{24}O_3$ 288.39	440.8		1.83	1.16
	17*α*-Ethinylestradiol (EE2) 57-63-6 ≥ 98.0%	$C_{20}H_{24}O_2$ 296.41	11.3		2.14	2.58
Alkylphenol	4-tert-octylphenol (4-t-OP) 140-66-9 ≥ 97.0%	$C_{14}H_{22}O$ 206.33	4.82		1.67	4.01
	Nonylphenol (NP) 84852-15-3 analytical standard	$C_{15}H_{24}O$ 220.36	7.62		0.78	1.96
Bisphenol	Bisphenol-A (BPA) 80-05-7 ≥ 99.0%	$C_{15}H_{16}O_2$ 228.29	120		0.61	2.79

a MDL for DGT sample: method detection limits of DGT samples calculated based on 7 days deployment in 15 ℃ (the average temperature of the sampling period)

Table S2: Concentration range, average and median concentration and the detection frequencies (Freq, %) of the TOrCs in raw influent, primary effluent, secondary effluent and final effluent from 10 WWTPs (n=30).

	Raw Influent (ng/L)				Primary Effluent (ng/L)				Secondary Effluent (ng/L)				Final Effluent (ng/L)			
	Range	Mean	Median	Freq /%	Range	Mean	Median	Freq /%	Range	Mean	Median	Freq /%	Range	Mean	Median	Freq /%
MEP	55.3-899	499	506	100	22.2-565	148	65.0	100	14.7-38.5	26.9	26.7	100	5.20-41.4	21.6	19.2	100
ETP	43.1-188	123	130	100	20.8-118	56.8	53.1	100	8.58-40.8	22.5	22.0	100	< MDL-47.1	14.3	9.86	97
PRP	72.9-564	314	303	100	29.7-421	138	91.0	100	14.6-109	42.1	29.4	100	8.12-109	39.9	31.9	100
UBP	4.84-32.3	21.5	22.6	100	< MDL-23.2	6.78	4.74	60	< MDL-3.40	< MDL	< MDL	7	< MDL	< MDL	< MDL	0
BEP	< MDL-29.2	6.06	3.86	60	< MDL-14.9	5.09	6.28	60	< MDL-9.02	2.64	< MDL	30	< MDL-5.02	< MDL	< MDL	20
HEP	< MDL-5.91	3.14	3.54	67	< MDL-4.55	< MDL	< MDL	10	< MDL	< MDL	< MDL	0	< MDL	< MDL	< MDL	0
PHBA	20.1-125	50.3	42.0	100	9.77-206	56.7	34.7	100	14.5-90.0	37.6	31.4	100	14.6-95.3	47.2	46.7	100
BHA	6.06-79.8	37.0	30.9	100	5.48-85.0	28.6	23.3	100	< MDL-67.6	22.6	19.1	80	< MDL-61.58	20.9	12.4	70
BHT	53.7-370	181	153	100	< MDL-597	200	150	77	< MDL-267	106	105	67	< MDL-502	113	< MDL	50
BPA	649-3639	1797	1747	100	252-2419	1268	1316	100	61.6-1532	578	458	100	< MDL-1450	490	354	90
DES	< MDL-15.7	6.08	5.69	70	< MDL-15.0	5.09	< MDL	50	< MDL-18.7	4.25	< MDL	40	< MDL-17.1	4.19	< MDL	40
E1	19.0-393	73.3	43.2	100	1.26-72.1	26.7	21.8	100	1.45-11.1	4.77	3.15	100	< MDL-22.8	5.87	< MDL	87
E2	7.09-49.9	22.4	19.2	100	3.30-256	32.5	12.4	100	2.90-14.4	6.39	5.51	100	< MDL-17.3	6.40	5.77	77
E3	17.4-215	79.1	67.1	100	< MDL-95.5	24.5	15.4	77	< MDL 15.6	2.93	< MDL	10	< MDL-18.9	3.20	< MDL	10
EE2	< MDL-18.7	< MDL	< MDL	20	< MDL-15.3	4.96	< MDL	30	< MDL-18.6	< MDL	< MDL	20	< MDL-14.9	< MDL	< MDL	10
OPP	13.1-276	110	93.0	100	10.1-123	44.9	35.4	100	< MDL-76.3	27.6	26.0	97	< MDL-83.1	27.5	21.9	80
TCS	15.9-278	136	120	100	20.0-349	112	63.1	100	6.65-159	67.0	64.9	100	< MDL-140	56.4	48.9	90
TCC	10.8-279	110	85.4	100	25.2-282	100	63.2	100	8.37-180	78.1	67.4	100	8.48-265	67.7	43.8	100
4-*t*-OP	< MDL-1588	446	329	77	< MDL-1854	504	357	70	< MDL-1004	310	228	67	< MDL-1257	308	297	60
NP	440-2437	1165	1101	100	167-2879	1092	1065	100	98.5-1376	565	492	100	134-1143	586	541	100

Table S3: Concentrations of TOrCs in the raw influent and final effluent from Wuhan and Dalian, and the significant differences (p=0.05, n=5).

	Raw Influent (ng/L)					Final Effluent (ng/L)				
	Wuhan		Dalian		significance	Wuhan		Dalian		significance
	Range	Mean	Range	Mean		Range	Mean	Range	Mean	
MEP	226-810	532	55.3-900	465	0.416	12.4-38.7	24.2	5.20-41.8	18.9	0.159
ETP	68.7-174	128	43.1-188	118	0.517	3.32-23.7	9.70	< MDL-47.1	19.2	0.0355
PRP	148-511	312	72.9-564	315	0.956	8.12-71.8	38.6	14.8-109	41.3	0.786
UBP	9.77-32.2	22.8	4.84-29.6	20.2	0.358	< MDL	< MDL	< MDL	< MDL	-
BEP	< MDL -11.64	4.76	< MDL -29.2	7.35	0.306	< MDL -5.02	< MDL	< MDL -4.73	< MDL	0.934
HEP	< MDL -5.91	3.62	< MDL -5.39	2.73	0.126	< MDL	< MDL	< MDL	< MDL	-
PHBA	20.1-66.8	40.8	27.2-125	59.9	0.039	14.6-66.4	38.8	26.0-95.3	56.2	0.019
BHA	20.43-79.8	38.0	6.06-65.1	36.0	0.776	< MDL -38.0	15.5	< MDL -61.6	26.7	0.123
BHT	53.7-234	106	116-370	257	0.000	< MDL -183	39.3	< MDL -502	192	0.001
BPA	649-3639	1863	1228-2177	1731	0.592	< MDL -928	283	96.4-1550	711	0.007
DES	< MDL -11.5	3.84	4.45-15.7	8.31	0.001	< MDL	< MDL	< MDL -17.1	6.99	0.000
E1	26.5-393	108	19.0-61.0	38.5	0.017	1.58-22.8	8.16	< MDL -11.1	3.41	0.045
E2	14.6-49.8	26.2	7.09-36.3	18.7	0.038	< MDL -16.3	6.67	< MDL -17.3	6.12	0.757
E3	39.1-215	99.5	17.4-123	58.7	0.022	< MDL	< MDL	< MDL -18.9	4.96	0.064
EE2	< MDL -18.7	< MDL	< MDL -10.3	< MDL	0.380	< MDL	< MDL	< MDL	< MDL	0.085
OPP	77.1-276	152	13.1-95.6	68.2	0.000	8.10-83.1	33.1	< MDL -56.4	21.5	0.169
TCS	60.3-267	144	15.9-95.4	128	0.561	< MDL -140	57.4	1.27-140	55.2	0.909
TCC	56.9-207	96.8	10.8-279	123	0.308	23.86-74.6	43.5	8.48-265	93.6	0.015
4-t-OP	< MDL -1109	317.7	< MDL -1589	575	0.095	< MDL -609	188	< MDL -1257	437	0.045
NP	440-2437	1086	478-1925	1245	0.412	179-1143	580	134-1140	592	0.210

Table S4: Concentrations of TOrCs in the raw influent and final effluent from Urban and Sub-urban areas, and the significant differences (p=0.05, n=5).

	Raw Influent (ng/L)					Final Effluent (ng/L)				
	Urban		Sub-urban		significance	Urban		Sub-urban		significance
	Range	Mean	Range	Mean		Range	Mean	Range	Mean	
MEP	301-900	604.59	55.3-760	392.66	0.007	11.4-41.4	26.22	5.20-43.9	17.23	0.015
ETP	98.4-188	143.96	43.1-151	102.58	0.003	3.32-47.1	18.82	< MDL -23.7	10.04	0.053
PRP	229-564	379.13	72.9-511	248.20	0.004	27.7-109	49.92	8.12-71.8	30.56	0.042
UBP	20.4-32.3	26.70	4.84-27.7	16.20	0.000	< MDL	< MDL	< MDL	< MDL	-
BEP	< MDL -29.2	6.72	< MDL -11.6	5.40	0.605	< MDL -5.02	2.56	< MDL	< MDL	0.003
HEP	< MDL -5.39	3.82	< MDL -5.91	2.53	0.023	< MDL	< MDL	< MDL	< MDL	-
PHBA	20.1-73.3	40.60	35.0-125	60.04	0.036	14.6-95.3	55.93	23.6-66.4	39.07	0.023
BHA	27.2-65.1	41.42	6.06-79.8	32.52	0.020	20.0-61.6	37.99	< MDL -12.4	4.94	0.000
BHT	53.7-370	207.04	66.8-351	155.63	0.164	< MDL -502	154.30	< MDL -218	74.02	0.103
BPA	649-3639	1955.21	900-2267	1638.28	0.194	96.4-1326	579.90	< MDL -1450	405.89	0.303
DES	< MDL -15.7	5.95	< MDL -11.5	6.21	0.859	< MDL -10.7	4.61	< MDL -17.08	3.80	0.603
E1	34.8-393	93.54	19.0-103	53.01	0.179	1.98-22.8	10.16	< MDL -4.21	1.86	0.000
E2	14.6-36.3	21.18	7.09-49.8	23.65	0.511	< MDL -17.3	8.18	< MDL -11.1	4.74	0.044
E3	48.0-123	75.04	17.4-215	83.09	0.665	< MDL -18.9	4.96	< MDL	< MDL	0.064
EE2	< MDL -18.7	5.84	< MDL	< MDL	0.020	< MDL	< MDL	< MDL -14.9	4.91	0.082
OPP	71.5-168	97.69	13.1-276	122.97	0.258	16.8-63.9	36.73	< MDL -83.1	18.84	0.030
TCS	85.8-278	190.42	15.9-135	81.65	0.000	53.2-140	101.32	< MDL -48.9	14.43	0.000
TCC	55.7-249	130.28	10.8-207	89.45	0.105	34.8-265	83.76	9.48-176	52.71	0.144
4-*t*-OP	< MDL -1589	457.57	< MDL -1109	434.90	0.886	< MDL -1257	493.01	< MDL -540	136.19	0.003
NP	930-1531	1141.61	440-2437	1189.34	0.807	359-1143	761.84	134-983	421.89	0.003

Table S5: Overall removal efficiency of TOrCs for 10 WWTPs (%).

	W1	W2	W3	W4	W5	D1	D2	D3	D4	D5
MEP	95.3 ±1.4	92.5 ±1.4	95.8 ±0.9	97.8 ±0.3	93.5 ±1.7	98.1 ±0.6	97.8±0.9	85.6 ±8.4	94.3 ±0.7	93.5 ±0.2
ETP	95.2 ±2.2	87.9 ±4.5	95.7 ±1.9	95.0 ±0.5	86.4 ±1.9	85.7 ±6.5	95.5 ±4.0	83.5 ±7.2	74.7 ±2.7	87.2 ±1.4
PRP	86.9 ±3.7	63.8 ±3.2	89.0 ±0.7	97.5 ±0.6	86.5 ±1.7	94.7 ±1.3	90.9 ±2.8	81.4 ±6.8	78.6 ±2.7	82.5 ±4.2
UBP	100	100	100	100	100	100	100	100	100	100
BEP	4.6 ±19.1	100	NA[a]	NA	100	80.3 ±5.1	100	NA	NA	100
HEP	100	NA	100	100	100	100	NA	NA	100	100
PHBA	-56.7 ±26.3	-5.5 ±50.6	5.5 ±53.8	6.4 ±8.4	45.1 ±11.7	10.7 ±16.8	37.2 ±9.3	53.8 ±6.8	-88.7 ±84.1	-13 ±59.0
BHA	18.9 ±16.9	64.4 ±6.7	-15.9 ±21.6	100	72.1 ±7.0	-4.5 ±25.4	100	100	5.2 ±15.6	32.8 ±28.4
BHT	-71.3 ±96.5	100	100	100	100	100	42.8 ±23.0	-43.9 ±40.4	12.6 ±16.9	-39.2 ±16.1
BPA	78.2 ±3.24	100	75.1 ±20.1	90.7 ±0.6	84.4 ±12.4	93.5 ±2.0	77.9 ±6.8	24.5 ±23.9	34.1 ±10.2	57.5 ±13.6
DES	NA	100	NA	100	NA	-12.2 ±42.3	100	-85.1 ±46.1	35.6 ±13.3	14.7 ±19.6
E1	43.8 ±8.5	96.3 ±0.6	95.5 ±1.7	97.4 ±1.0	93.0 ±1.8	93.5 ±2.0	97.0 ±2.7	100	75.9 ±4.8	95.0 ±0.9
E2	28.5 ±26.6	71.7 ±8.4	100	86.1 ±2.5	74.7 ±11.1	78.1 ±4.4	100	71.8 ±27.1	35.8 ±6.3	53.7 ±23.9
E3	100	100	100	100	100	100	100	100	80.5 ±4.9	100
EE2	NA	NA	100	NA	NA	100	NA	NA	NA	NA
OPP	86.5 ±3.9	83.9 ±1.2	37.0 ±7.7	95.0 ±0.2	67.8 ±13.8	74.2 ±9.8	100	100	46.6 ±5.5	49.8 ±2.5
TCS	44.8 ±3.6	58.9 ±1.0	47.4 ±13.6	100	71.5 ±2.9	43.5 ±7.9	97.6 ±0.9	71.9 ±8.6	47.5 ±13.2	43.8 ±23.3
TCC	37.0 ±17.1	52.7 ±4.9	19.3 ±35.4	74.8 ±5.5	60.1 ±6.9	40.6 ±10.5	-35.0 ±22.8	19.6 ±5.6	34.7 ±14.0	17.6 ±49.3
4-*t*-OP	-35.1 ±18.9	100	NA	NA	51.4 ±17.3	-51.8 ±106	100	12.3 ±38.8	-157 ±269.7	15.3 ±48.5
NP	11.8 ±25.2	56.5 ±3.4	56.8 ±6.9	48.0 ±4.3	51.4 ±15.5	36.4 ±14.2	81.8 ±12.7	69.1 ±7.1	40.4 ±5.5	11.1 ±11.8

a NA: not applicable

Table S6: Average mass loadings and emissions of TOrCs per inhabitant for the people served by 10 WWTPs (μg/d/inhabitant).

		W1	W2	W3	W4	W5	D1	D2	D3	D4	D5
Mass Loading	Preservatives	399	98.3	471	641	167	442	133	63.4	164.3	280
	Antioxidants	39.7	19.9	42.2	82.1	34.5	90.1	46.5	27.1	38.5	130
	Oestrogens	43.1	42.6	185	152	17.8	49.8	13.4	11.1	19.6	51.2
	Disinfectants	124	50.1	200	236	57.4	73.3	42.1	10.7	61.3	173
	BPA	440	398	487	332	231	409	418	176	191	852
	Alkyl-phenols	1021	169	505	946	321	496	270	274	206	656
	Total TOrCs	2067	778	1889	2388	829	1560	922	562	681	2142
Emission	Preservatives	46.2	23.4	40.2	37.4	19.8	35.6	10.3	16.0	30.7	57.4
	Antioxidants	53.9	3.50	22.2	6.43	3.05	19.5	23.0	34.7	33.2	168
	Oestrogens	12.0	4.84	9.15	6.38	2.13	5.07	1.27	3.39	5.67	9.72
	Disinfectants	51.6	15.9	118	26.3	17.9	34.2	24.8	3.30	34.4	111
	BPA	441	152	211	173	110	343	54.2	82.21	167	699
	Alkyl-phenols	224	0.08	99.1	87.8	50.9	30.9	58.8	202.7	134	283
	Total TOrCs	829	200	499	337	204	469	172	342	405	1329

Table S7: Significant differences (p=0.05, n=15) of mass loading and emission between Wuhan and Dalian, urban area and sub-urban area.

	Mass Loading				Mass emission			
	Total		Per inhabitant		Total		Per inhabitant	
	Wuhan/Dalian	Urban/ Sub-urban	Wuhan/Dalian	Urban/ Sub-urban	Wuhan/Dalian	Urban/ Sub-urban	Wuhan/Dalian	Urban/ Sub-urban
MEP	0.068	0.000	0.021	0.054	0.061	0.001	0.002	0.002
ETP	0.096	0.000	0.026	0.022	0.245	0.000	0.106	0.002
PRP	0.182	0.000	0.117	0.084	0.368	0.000	0.248	0.000
UBP	0.066	0.000	0.022	0.012	-	-	-	-
BEP	0.999	0.012	0.250	0.140	0.160	0.005	0.375	0.001
HEP	0.048	0.000	0.029	0.151	-	-	-	-
PHBA	0.215	0.000	0.981	0.597	0.517	0.000	0.941	0.016
BHA	0.320	0.000	0.157	0.547	0.807	0.000	0.799	0.000
BHT	0.227	0.000	0.007	0.024	0.677	0.001	0.046	0.064
BPA	0.093.	0.005	0.054	0.103	0.470	0.001	0.268	0.061
DES	0.041	0.000	0.043	0.484	0.064	0.000	0.002	0.142
E1	0.044	0.011	0.029	0.124	0.044	0.004	0.007	0.001
E2	0.082	0.000	0.035	0.950	0.322	0.005	0.325	0.059
E3	0.042	0.001	0.016	0.666	0.281	0.001	0.264	0.008
EE2	0.098	0.001	0.144	0.030	0.013	0.000	0.001	0.387
OPP	0.006	0.018	0.000	0.805	0.066	0.000	0.055	0.005
TCS	0.096	0.000	0.019	0.001	0.161	0.000	0.253	0.000
TCC	0.921	0.000	0.578	0.291	0.893	0.000	0.468	0.046
4-*t*-OP	0.817	0.018	0.104	0.221	0.992	0.001	0.131	0.002
NP	0.273	0.000	0.369	0.024	0.332	0.000	0.413	0.000

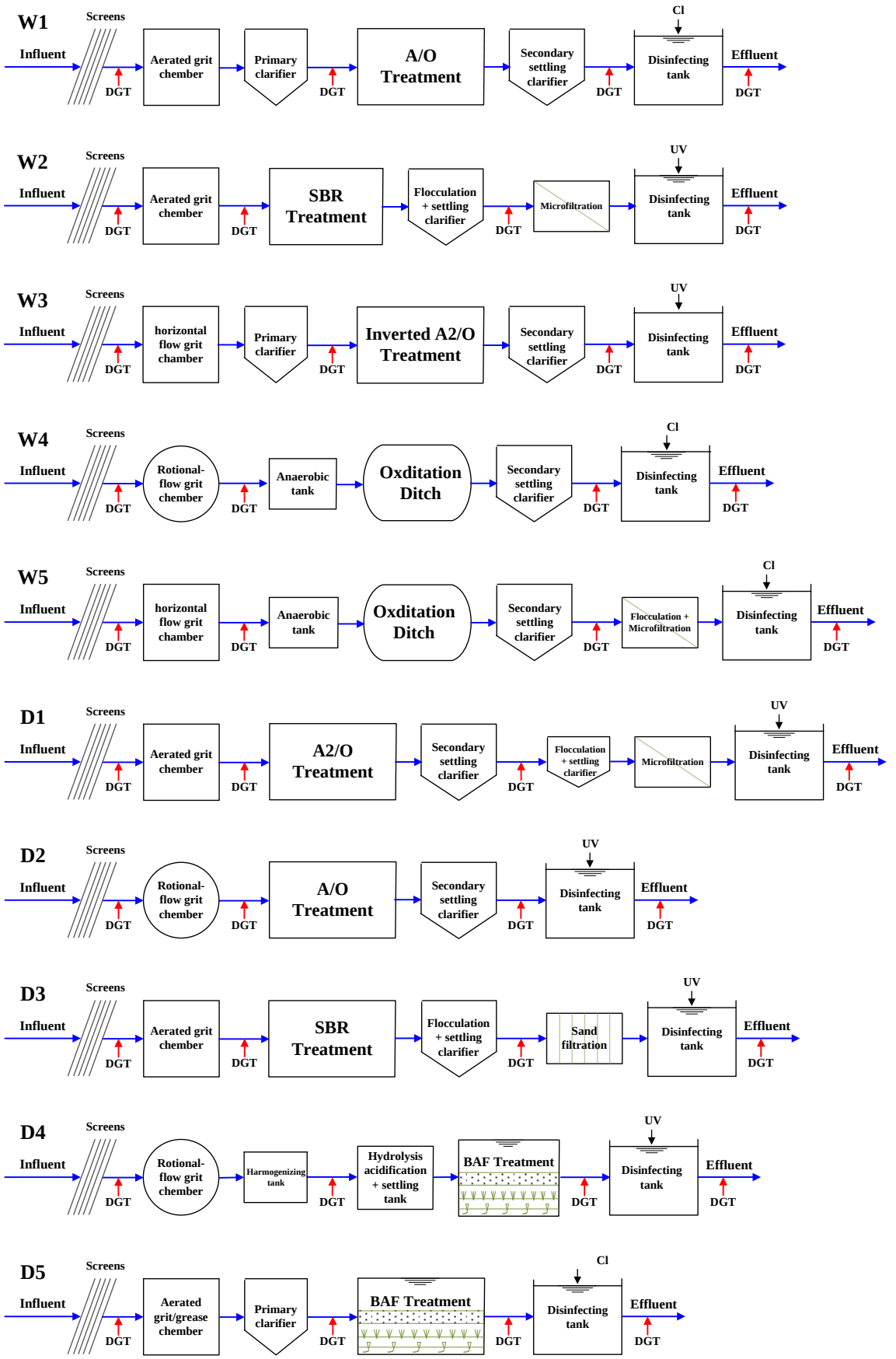


Figure S1: Schematic diagrams of the main water flow and DGT deployment sites for the 10 selected WWTPs.

Appendix I

Co-authored article in *Talanta*, 2015, 132: 902-908:

In situ Measurement of Solution Concentrations and Fluxes of Sulfonamides and Trimethoprim Antibiotics in Soils using o-DGT

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In situ measurement of solution concentrations and fluxes of sulfonamides and trimethoprim antibiotics in soils using o-DGT

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ABSTRACT

Techniques, such as Diffusive Gradients in Thin-films (DGT), which either minimally disturb the soil or perturb it in a controlled way are most likely to provide information relevant to toxicity. Herein, we report the first use of DGT for organics (o-DGT) in soil systems to gain insight into the mobility and lability of four antibiotics—sulfamethoxazole (SMX), sulfamethazine (SMZ), and sulfadimethoxine (SDM), trimethoprim (TMP) in soil. In experiments where the same known amount of antibiotics were spiked into the soil, which was then further modified with NaOH, NaCl or dissolved organic matter, directly measured soil solution concentrations (C_{soln}) of these antibiotics were in the order: SMX > SMZ ≈ SDM > TMP. The *R* values (ratio of concentrations measured by o-DGT and directly in solution) were 0.56, 0.41, 0.40 and 0.28, respectively, indicating that the removal of these antibiotics from the solution can be to some extent resupplied by release from the solid phase. The nonlinearity of the relationship between o-DGT fluxes and the reciprocal of diffusive layer thickness (Δg) also suggested that soil solution concentrations were only partially sustained by the solid phase. The potential fluxes of these antibiotics in this soil were 5.4, 3.6, 2.4, and 1.2 pg/cm^2/s for SMX, SMZ, SDM, and TMP, respectively. o-DGT is a promising tool for understanding the fate and behaviour of polar organic chemicals in soil, and it potentially provides an *in situ* approach for assessing their bioavailability.

1. Introduction

Antibiotics are one of the most important classes of pharmaceuticals, widely used in our daily life, for human and veterinary purposes to cure or prevent some bacteria associated diseases. As some of the dose of antibiotics administered to animals or humans is not metabolized, it is excreted and enters effluent streams and reaches the environment [1]. Antibiotics are incompletely removed by wastewater treatment plants (WWTPs) [2], and discharged as parent compounds or easily re-transferable metabolites. Their adverse effects, particularly promotion of antibiotic resistance [3], has raised their profile within environmental science and ecology as a problem contaminant [4]. Antibiotics could enter the soil system through sludge/manure application or effluent irrigation. However, although these rather polar organic compounds have been in use for over half a century, knowledge of their fate and behaviour in soil systems is still not fully understood [5,6].

Understanding the interactions between contaminants and soils is essential for their risk assessment. Currently, there is a lack of understanding of both chemical speciation in soil solution and the kinetics of exchange between solution and solid phase. Most of the current knowledge on the environmental behaviour of antibiotics in soils has been gained by batch [6–13] or dynamic column [14,15] studies. While the information provided by such procedures is useful, information it does not relate directly to the *in situ* transfer of antibiotics between solids and solution, even though it is this *in situ* information which is essential for understanding their bioavailability/mobility and developing predictive models. Traditional approaches such as chemical extraction disrupt chemical equilibria, which may affect the distribution of species in solution, while dynamic column techniques also change soil conditions from the natural *in situ* situation. *In situ* chemical measurements which either minimize disturbance or perturb the solution in a controlled way [16] offer an alternative approach.

Recently we developed a novel passive kinetic sampler—Diffusive Gradients in Thin-films for organics (o-DGT) to measure antibiotics in solutions *in situ* [17]. It has been successfully employed to measure the concentrations of antibiotics in WWTP [18]. The DGT technique has been successfully and widely used to assess the availability, toxicity and lability of inorganic chemicals in soils and sediments [19,20]. In the present study, availability

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refers to all the fraction of chemicals that can be accumulated by o-DGT, while lability particularly is used in reference to the susceptibility of a compound to desorption from soil particles. Most studies using passive equilibrium samplers to investigate availability/toxicity [21,22] in soil/sediment have been focused on persistent organic pollutants (POPs), with little work on polar organic chemicals (POCs). To start to fill this knowledge gap, we applied the o-DGT technique to soils and present the first measurements by o-DGT of antibiotics in a soil system. This study was performed on soils in which sodium azide (NaN_3) was added to inhibit the microbial activity [23], to facilitate investigation of physico-chemical processes.

2. Theory of o-DGT

The DGT technique is based on Fick's first law of diffusion [24]. A resin layer is separated from bulk solution (with a concentration C) by an analyte-permeable diffusion layer of thickness Δg, comprising an agarose or polyacrylamide hydrogel, known as the diffusive gel, plus a filter membrane (Fig. 1). Analyte diffuses through the diffusion layer (with a diffusion coefficient D) and is rapidly bound by the resin in the binding gel. For well stirred solutions or a hypothetical fully sustained sediment/soil (see fully supplied case (i) later), C is constant outside the o-DGT unit and a constant concentration gradient is maintained in the diffusion layer during the deployment time (t) (case (i) in Fig. 1). The flux (F) of analyte diffusing through the diffusion layer is determined by Eq. (1):

$$F = \frac{DC}{\Delta g} \quad (1)$$

In practice, the flux of an analyte from soil to an o-DGT device can be calculated from the measured mass (M) accumulated during the deployment time through a well-defined exposure area (A) (Eq. (2)). This assumption of a steady state flux requires that capacity of the binding layer is not approached. A high capacity that fulfils this condition has been established [17]:

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

In soil systems, the flux from the solid phase to solution, F_{ss}, induced by o-DGT may not be the same as the potential maximum flux from the solid phase to solution, F_m. Depending on the characteristics of the o-DGT device and the soil properties, F_{ss} will be a fraction of F_m and is therefore regarded as a partial flux. The directly measured o-DGT flux (F_{DGT}) of analyte from the solid phase to solution and its relationship to F_{ss} and F_m can be considered for three possible conditions [16] (Fig. 1).

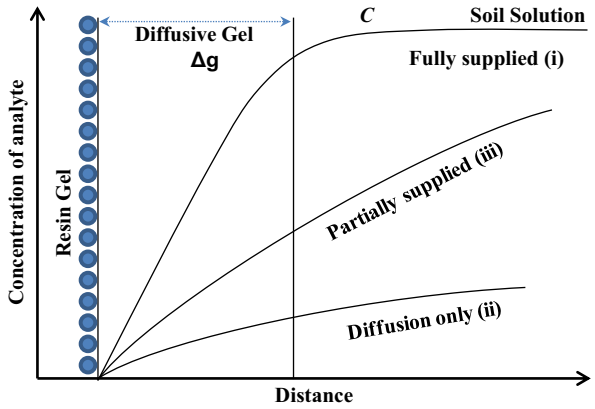


Fig. 1. Schematic of concentration gradients in o-DGT and soil.

2.1. Fully supplied

This is typically the case in well stirred solutions where C is independent of the distance from the membrane. In soils or sediments, analyte taken up from the pore water by the o-DGT is rapidly resupplied from the solid phase provided there is a labile pool size, which results in an effective buffer to maintain a constant concentration in the pore water. In this case, the concentration in soil solution or pore water can be calculated by Eq. (3):

$$C = \frac{M\Delta g}{DAt} \quad (3)$$

The F_{DGT} can be calculated by Eq. (2). It is likely to be less than F_m as the flux could be higher if an o-DGT device with a different geometry and higher demand for the analyte was used.

2.2. Diffusion only

There is no resupply from the solid phase to the soil solution *i.e.* $F_{ss} \approx 0$. The only supply of analyte to a DGT device is diffusion. The concentration in the soil solution at the surface of the device will gradually decline, with this depletion in concentration progressively extending further into the soil away from the surface of the o-DGT device, resulting in a concentration gradient in the soil. Consequently F_{DGT} declines with deployment time.

2.3. Partially supplied

There is some re-supply of analyte from the solid phase to solution, but it is insufficient to sustain the initial concentration in the soil solution and to satisfy the DGT demand. In this case, $F_{ss} \approx F_{DGT} \approx F_m$.

In general, case (iii) is the most likely and expected phenomena, particularly for organic chemicals, which may be supplied from the solid phase to solution by breaking the forces of various interactions, including electrostatic, surface complexation and hydrogen bonding [25]. Case (i) and (ii) are two extremes for soils and sediments, but they may be approached.

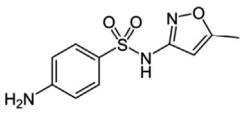
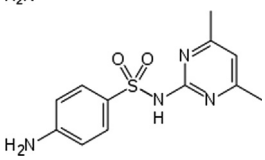
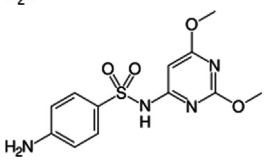
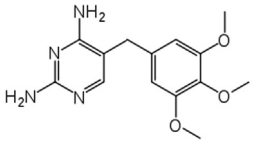
The ratio (R) of o-DGT measured concentration (C_{DGT}) to the independently measured soil solution concentration (C_{soln}) is an indicator of the extent of depletion of solution concentrations at the DGT interface (Eq. (4)) [26]:

$$R = \frac{C_{DGT}}{C_{soln}} \quad (4)$$

R can help identify the different cases mentioned above. If $R=1$ (in practice, $R \geq 0.95$), then the analyte in the soil solution is fully supplied by the solid phase. If $0.1 < R < 0.95$, then it is partially supplied. If $R < 0.1$, it would be seen as diffusion only case, with no resupply from the solid phase to the solution. Generally higher R values indicate that the labile pool size of the analyte is large and/or a fast resupply rate.

The above mentioned cases can also be identified using approaches that do not rely on the measurement of R. Deployment of o-DGT devices with various thicknesses of diffusive layers (different Δg) for the same time can provide plots of fluxes against $1/\Delta g$, while deployments with a constant Δg for different times provide plots of fluxes versus time. In both cases the lines increase linearly with $1/\Delta g$ or time for the fully supplied case, but are curved for the partially supplied or diffusion only cases (Fig. S1).

Table 1
Physiochemical properties and chemical structures of antibiotics in this study

Compound	Structure	CAS	MW	S_W (mg/L)[a]	p$Ka_{1,2}$	logK_{ow}[b]
SMX		723-46-6	253.3	610	1.9, 5.6	0.89
SMZ		57-68-1	278.3	1500	2.1, 7.5	0.89
SDM		122-11-2	310.3	343	2.5, 5.9	1.63
TMP		738-70-5	290.3	400	3.2, 6.8	0.91

[a] Water solubility from Ref. [28].
[b] Obtained from EPI suite 4.0, USEPA.

3. Methods and materials

3.1. Chemicals

Four antibiotics—sulfamethoxazole (SMX, purity > 98%), sulfamethazine (SMZ, purity > 99%), sulfadimethoxine (SDM, purity > 98.5%), trimethoprim (TMP, purity > 99%) and ^{13}C-Caffeine (^{13}C-CAF as the internal standard [27], purity > 99%) were supplied by Sigma-Aldrich (Poole, UK). Their physiochemical properties are given in Table 1.

Antibiotic stock solutions were dissolved in pure methanol. Acetonitrile (ACN) and methanol (MeOH) were purchased from Fisher (Poole, UK). Humic acid (used as the dissolved organic matter—DOM) was obtained from the International Humic Substances Society.

3.2. Soil sample and treatments

The soil was collected from near Preston, Lancashire, U.K. The physico-chemical properties of this soil are: texture clay loam, maximum water holding capacity (MWHC) 46%, pH 6.5 (dH_2O), sand 56%, silt 25%, clay 19% and soil organic matter (SOM) 4.8% [29]. The soil was air dried and passed through a 2 mm sieve to remove roots and stones prior to experiments.

The soil was spiked with antibiotic solutions. Spiking solutions were prepared in methanol and added to soils, to deliver individual antibiotic concentration of 2.5 mg/kg in order to be detected in the solution. NaN_3 (10 mM) was added to inhibit the microbial activity [23]. To minimise solvent effects, the antibiotic solutions were first added to 25% of the soil and allowed to vent totally (to avoid potential effect of MeOH) before mixing well with the remaining soil (*i.e.* 75% of the soil) following the procedure in previous study [30]. Blank soil that was not augmented with antibiotics, but treated with the same amount of pure MeOH, was also prepared following the same procedure. The soils were then wetted to 50% MWHC by adding appropriate amounts of MQ water (high purity water, Milli-Q water system, UK), mixed well and left to equilibrate at room temperature. After 1, 2, 4, 7, 10, 15, and 19 days, soil was wetted to 100% MWHC 24 h before o-DGT deployment, and mixed well to obtain a soil slurry [16]. This pre-test established the time for reaching equilibrium and further experiments were conducted after 15 days equilibration. Soils were also modified using NaOH, NaCl and DOM to produce soils with different pH, ionic strength and organic matter for investigating their effects on fluxes from the solid phase to solution. In summary, six treatments were carried out. A, soil spiked with antibiotics; B, soil A mixed with blank soil (1:1) to produce soils with different antibiotic concentration; C, soil A further spiked with 0.01 M NaOH; D, soil A further spiked with 0.1 M NaOH; E, soil A further spiked with 0.1 M NaCl; F soil A further spiked 1.1% DOM. The resulting pH and SOM are given in Table 2.

3.3. o-DGT preparation and deployment

Standard o-DGT devices with 0.5 mm XAD18 resin gels, 0.8 mm agarose diffusive gels and polyethersulfone (PES) filter membranes were prepared as in our previous study [17]. o-DGT units were also made with different thicknesses of diffusive gels. The diffusive layer thickness including the PES filter ranged from 0.14 to 2.14 mm.

Deployment in the soil followed the standard procedures for using DGT in soils [16]. Briefly, a small amount of soil paste was applied gently onto the filter surface of the o-DGT devices and then pushed gently onto the soil surface with a slight twisting movement, enabling good contact between the soil and the device. All o-DGT devices were deployed for 24 h at room temperature (18 ± 3 °C). Photographs of laboratory deployment are provided in Fig. S2.

3.4. o-DGT retrieval and soil sampling

After deployment, o-DGT devices were retrieved. Soil particles were jet washed away with MQ water, the binding gel was removed (Fig. S2) and put into amber glass vials. An appropriate amount of internal standard was added. To extract the target chemicals 5 mL of MeOH was added into the vial followed by 20 min ultrasonication and the process repeated with a further 5 mL of MeOH. As recovery of all analytes was > 95%, 100% recovery was assumed in calculations [17].

Table 2
Concentrations (mean (SD)) of 4 antibiotics in soil solution and o-DGT measured fluxes in soils with various modifications ($n=3$).

Treatments[a]	BK	A	B	C	D	E	F
pH (dH_2O)	6.6	6.6	6.6	6.9	7.6	6.5	6.3
SOM	4.8%	4.8%	4.8%	4.8%	4.8%	4.8%	5.9%
Solution concentrations (ng/mL)							
TMP	0	24.5 (3.5)	9.93 (1.6)	23.5 (2.3)	26.3 (7.4)	28.9 (4.3)	28.4 (2. 6)
SMZ	0	196 (16.1)	106 (9.7)	189 (10.8)	196 (20.9)	182 (49.1)	219 (18.9)
SMX	0	519 (41.2)	267 (27.3)	506 (23.9)	655 (65.9)	456 (137)	587 (67.1)
SDM	0	203 (12.1)	94.1 (14.0)	212 (11.2)	410 (29.5)	175 (42.1)	222 (21.2)
Acetonitrile extract—C_s (ng/g, dw[b])							
TMP	0	839 (47)	348 (29)	806 (25)	884 (35)	936 (47)	840 (62)
SMZ	0	696 (14)	185 (40)	686 (62)	668 (41)	630 (19)	693 (95)
SMX	0	1754 (57)	649 (32)	1664 (103)	1608 (132)	1616 (75)	1815 (181)
SDM	0	2042 (45)	1067 (159)	1975 (63)	1852 (128)	1940 (30)	2143 (42)
Fluxes ($pg/cm^2/s$)							
TMP	0	0.44 (0.01)	0.22 (0.04)	0.48 (0.02)	0.54 (0.04)	0.55 (0.01)	0.51 (0.01)
SMZ	0	2.76 (0.15)	1.12 (0.19)	2.68 (0.13)	2.97 (0.03)	2.58 (0.08)	2.59 (0.07)
SMX	0	5.40 (0.17)	2.29 (0.36)	5.60 (0.36)	7.36 (0.34)	4.91 (0.12)	5.01 (0.32)
SDM	0	2.60 (0.14)	0.87 (0.13)	2.78 (0.19)	5.92 (0.06)	2.31 (0.05)	2.58 (0.08)

[a] BK, blank soil—no antibiotics added; A, spiked antibiotics, B, BK+A (1/1 w/w); C, A+0.01 M NaOH; D, A+0.1 M NaOH; E, A+0.1 M NaCl; F, A+1.1% DOM.
[b] Dry weight based.

The pooled extract was blown down to dryness with a gentle N_2 flow, reconstructed in 1 mL of MeOH, and filtered through 0.2 μm PP syringe filters (Pall, UK) into a 2 mL GC vial.

About 5 g of the soil slurry was sampled and centrifuged at 3000 rpm for 30 min to obtain soil solution. The solution was filtered (with 0.2 μm PP syringe filters, Pall, UK) into 1 mL glass vials. The rest of the soil was extracted twice with 10 mL acetonitrile (ACN) [10]. All the samples were reconstructed in initial mobile phases before being injected into the HPLC.

3.5. Chemical analysis

A Thermo Finnigan HPLC coupled with a photodiode array detector was employed to analyze the antibiotics by UV absorbance at 265 nm. A Varian Pursuit C18 LC column (150 × 2.1 mm, 3 μm) was used to separate antibiotics. The mobile phase used was: 0.2% formic acid in MQ water (A) and acetonitrile (B). The gradient procedure was optimised at: 0–1 min, 10% B, then increase to 70% B within 11 min, followed by increasing to 100% B in 1 min, hold for 5 min, after that decrease to the initial condition within 1 min. Finally, 10 min of post run ensured re-equilibration of the column before the next injection. The injection volume was 10 μL and the column temperature was set at 30 °C. The quantification of antibiotics was based on an internal standard method following a previous study [27], and the instrument detection limits were 1–5 ng/mL.

3.6. Quality assurance/control (QA/QC)

Blank soils without spiking antibiotics were analyzed and no target compounds were detected (Table 2). The caffeine (which might interfere with the internal standard analysis) was not detectable. Every batch of samples was analyzed in parallel with a standard solution and blank (initial mobile phase) to check the instrument performance. Values within 5% of the previous measurements were considered acceptable.

4. Results and discussion

4.1. Concentrations in soil solution

In a pilot experiment with sterile soils, soil solution concentrations (C_{soln}) decreased over the first 7 days after spiking, but changed insignificantly (ANOVA, $p > 0.05$, SPSS, IBM Statistics 20) after 7 days (Table S1). This indicates the added chemicals have reached equilibrium with the soils. Subsequent studies were conducted with soils allowed to equilibrate for 15 days.

Although the 4 antibiotics were spiked to the same concentration (*i.e.* 2.5 mg/kg), the C_{soln} varied between compounds (Table 2), with SMX the highest, followed by SDM, SMZ and TMP. C_{soln} for TMP was much lower than that for the three sulphonamides. Different from traditional soil-solution partition coefficient (K_d) which refers to the total solid phase concentration, this study uses labile soild phase-solution phase partition coefficient (K_{dl}) since the labile fraction in the soil particles was refered here, estimated by the ACN extraction. TMP has a higher K_{dl} than SMX, SMZ and SDM, and SMX has the lowest value, which is consistent with previous studies of K_d [10,31]. C_{soln} for SMZ was comparable to or slightly higher than for SDM, even though they have different logK_{ow} values of 0.89 and 1.63, respectively. These results suggested that chemical structure is an important factor affecting the fate of antibiotics in soil, different chemical structure results in different steric hindrance, p*K*a, etc. K_{ow} is not the only key parameter to contol the fate of these polar organic chemicals [25]. Mass balance estimates showed that nonextractable (ACN) fractions are (69 ± 8)%, (76 ± 8)%, (67 ± 9)%, and (60 ± 8)% for TMP, SMZ, SMX, and SDM, respectively.

4.2. Concentrations measured by o-DGT

The *D* values for these antibiotics, taken from a previous study [18], are 4.19E−06, 3.29E−06, 3.15E−06, and 3.11E−06 cm^2/s at 18 °C for SMX, SMZ, SDM, and TMP, respectively. The appropriate values were used in Eq. (3) in calculating concentrations measured by o-DGT (C_{DGT}). Like directly measured pore water concentrations they declined with aging time. *R* values for each antibiotic were obtained using Eq. (4).

For the aged soils, concentrations calculated from o-DGT correlated well with independently measured C_{soln} (Fig. 2). This results in averaged *R* values of 0.56, 0.41, 0.40, and 0.28 for TMP, SMZ, SDM, and SMX, respectively. The higher *R* value of TMP than the other three antibiotics at a given time indicates that it can be resupplied more quickly by the solid phase than SDM, SMZ and SMX and/or it has a larger labile reservoir.

A lower o-DGT concentration than that measured directly in soil solution indicates that the solution concentrations of these

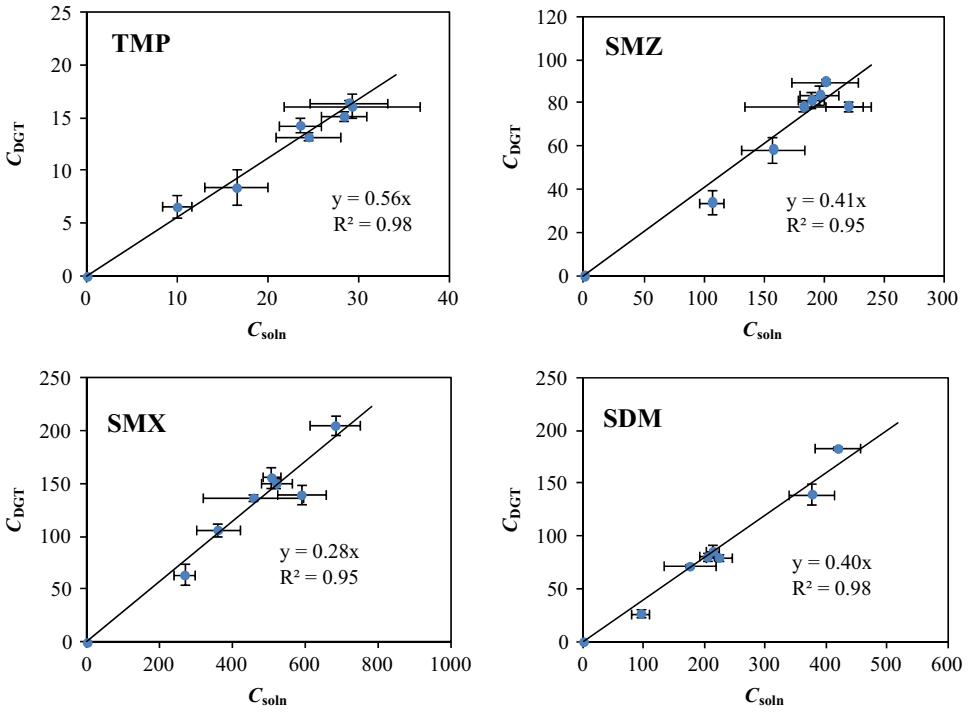


Fig. 2. Relationships between o-DGT measurement (C_{DGT}, ng/mL) and directly measured soil solution concentrations (C_{soln}, ng/mL) of 4 antibiotics in soils (error bars: SD for triplicate measurements).

antibiotics were only partially sustained by the solid phase [16]. The lower C_{DGT} than C_{soln} could be due to: (1) some species in the solution being unavailable to the o-DGT and/or (2) kinetic limitation of the resupply from the solid phase to soil solution. During deployment, the antibiotics at the surface of o-DGT devices were consumed, resulting in a decrease in the soil solution concentration at the interface. The removal of antibiotics in the solution at this interface could not be sufficiently rapidly resupplied by desorption from the solid phase. Consequently the concentration was depleted and the flux to the o-DGT device was less than the maximum possible flux, and the mean concentration measured by o-DGT, C_{DGT}, was lower than the initial solution concentrations, C_{soln}.

The acetonitrile extractable fraction was used here to estimate the labile solid phase concentrations in soil, and then K_{dl} could be derived. They were constant for each of the 4 antibiotics in the variously modified soil except for SDM in the soil at pH 7.6, for which the obtained K_{dl} (5.0) was only about half of the value obtained (10.6) for lower pH soils. As R was the same (0.40) for this higher pH soil, the desorption rate, k, must be larger. It appears that the desorption rate constant (and K_{dl}) is only sensitive to pH for SDM, whereas for TMP, SMZ and SMX it is independent of pH.

4.3. Fluxes from solid phase to solution

As discussed above, in most cases, these antibiotics in this soil solution are partially sustained by resupply from the solid phase. Therefore, the o-DGT results should be interpreted as fluxes rather than concentrations. The calculated, time-averaged, fluxes to o-DGT (F_{DGT}) are approximately equal to the average fluxes from solid phase to solution induced by o-DGT (F_{ss}) (given in Table 2).

Environmental changes (such as irrigation and application of manure or sludge) in the soil system will change soil properties (*e.g.* pH, cation exchange capacity—CEC and soil organic matter—SOM) which will consequently lead to different flux responses of these antibiotics from soil particles to soil solution. Fig. 3 shows the effect of soil pH on the fluxes of these 4 antibiotics from solid phase to solution. Good correlations were observed between the fluxes and soil pH (6.3–7.6). Less sensitivity of the fluxes for TMP and SMZ to pH might be due to the pH values studied being within (nearly all for SMZ and partly for TMP) the range of pKa_1 to pKa_2 (Table 1), where there are no big changes in the speciation. Increasing pH appears to facilitate the fluxes from solid phase to solution, which is consistent with previous studies [6,7,25]. At higher pH there is a greater proportion of anionic species, resulting in higher electrostatic repulsion between anionic sulphonamides and the negatively charged soil surface. Increasing soil pH leads to remobilizing the antibiotics, raising the risks of these antibiotics in terms of exposure to microorganisms or contamination of ground water.

Ionic strength and SOM affect sulphonamides and TMP differently. Both increasing of the ionic strength and SOM enhanced ($p < 0.05$) fluxes of TMP from the solid phase to the solution (Table 2). This could be due to the decreasing thickness of the electrical double layer of the charged surface [6] and competition between SOM and TMP [32]. However, it seems that both ionic strength and SOM suppressed slightly the fluxes of sulphonamides (SMZ, SMX and SDM) from soil particles, although not significantly for the SOM effect. The ionic strength effect in this study for SAs is inconsistent with a study by Białk-Bielińska and co-workers [6], where they found increasing ionic strength decreased the K_d of SAs. This might be attributed to the different composition of the exchangeable cations [7,32].

Deployment of o-DGT with different thicknesses of diffusive gel layers can help to characterize the transport of antibiotics from soil solids to solutions. For example, o-DGT with 0.8 mm and 0.5 mm diffusive gels were deployed in the soils for the same time. If concentration measured by o-DGT with 0.8 mm gel was higher than that by o-DGT with the 0.5 mm gel, it indicates the antibiotic in the soil solution was partially supplied by the solid phase. Obtaining lower C_{DGT} with thinner gels (0.5 mm) than thicker ones (0.8 mm) implies resupply from the solid phase cannot satisfy the demand of the uptake of o-DGT with a 0.5 mm gel, hence the solution is only partially resupplied due to limited labile pool or/and kinetic limitation. This is consistent with the observations made by comparing C_{DGT} with C_{soln} (R values).

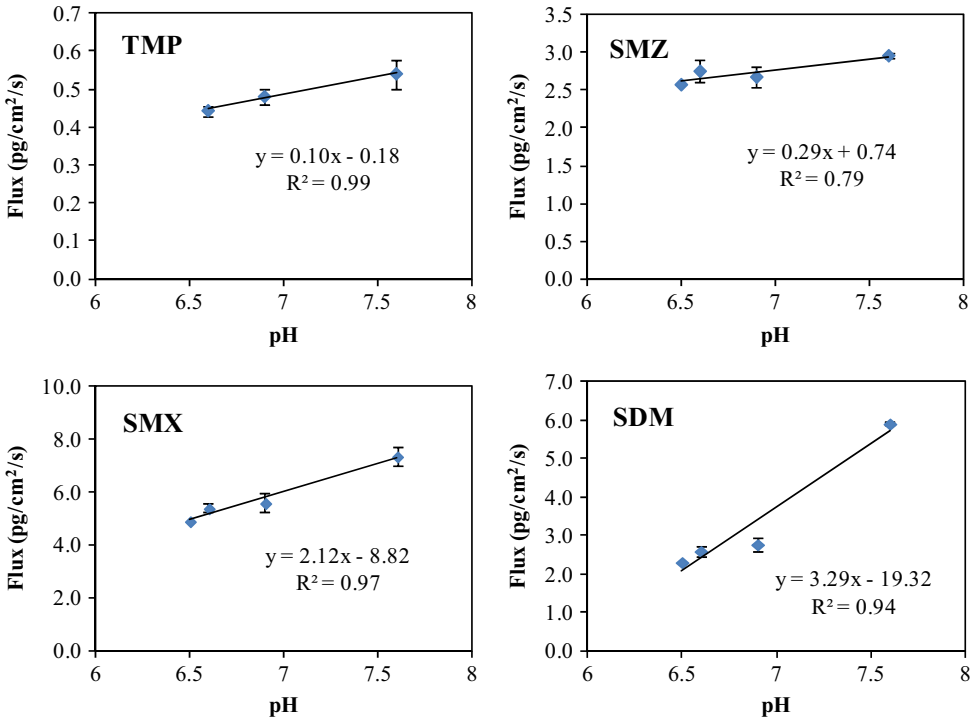


Fig. 3. Relationships between fluxes of antibiotics from solid phase to solution and soil pH (error bars: SD for triplicate measurements).

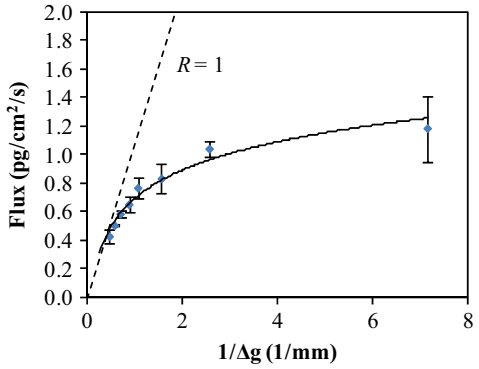


Fig. 4. o-DGT Fluxes of TMP *vs* reciprocal of diffusive layer thickness in the clay loam soil (dash line represents theoretical line according to Eq. (1) where $R=1$; error bars: SD for duplicate measurements).

Deployment of o-DGT with various thicknesses of diffusive gel layers can offer further information (Fig. 4). A nonlinearity of the plot of flux against the $1/\Delta g$ again suggests the concentrations of these antibiotics in the soil solution were partially supplied by desorption from the soil particles. A straight line interpretable with a slope of *DC* would only be expected if there was full supply from the solid phase (no kinetic limitation), where *R* should be 1 (shown in Fig. 4, TMP as an example). Although the demand for the o-DGT with thicker diffusion layers was smaller, it could not be satisfied by the resupply from the solid phase, as shown by the data points being lower than the $R=1$ line. Lower values than the theoretical slope and the apparent approach to a plateau suggest a kinetic limitation on the supply from solid phase to solution.

Deployments of o-DGT with thicker diffusion layers than those used here might enable accurate measurement of slope, *DC*, and derivation of the solution concentration, facilitating quantitative comparison with *R*. Fluxes of o-DGT with the thinnest diffusive layer are limited by the supply from soil to solution and so give potential fluxes of these antibiotics from this soil. The values were 5.4, 3.6, 2.4, and 1.2 pg/cm^2/s for SMX, SMZ, SDM and TMP, respectively. The fluxes measured using the standard o-DGT (0.8 mm diffusion gel) are about 60% for TMP and 80% for sulphonamides of the potential fluxes.

5. Conclusions and environmental implications

An important finding of this work is that when antibiotics are removed from solution, as they might be by biota, they are to an extent rapidly supplied by the solid phase. This resupply is most significant for SMX and least for TMP. Values obtained for the potential maximum supply fluxes of each antibiotic from soil to solution have the potential to be used in models of biological uptake. They could be used to estimate maximum possible uptake, as limited by transport form the soil.

This work has demonstrated that o-DGT is an *in situ* technique, which can provide quantitative measurements of antibiotic remobilization fluxes from soil to soil solution, and this might be linked to their bioavailability. DGT measured fluxes of metals have proved to be a good surrogate for plant uptake [19]. There is an urgent need to establish whether the bioavailability of antibiotics in soil/sediment can be predicted by o-DGT measurements. o-DGT opens up the possibilities of both directly obtaining kinetic information of polar organic chemicals such as antibiotics in natural or contaminated soil/sediment systems and providing an *in situ* measurement of bioavailability. In doing so it is likely in the future to enhance our understanding of the behaviour of these organic chemicals in the environment and improve risk assessment and associated models.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2014.08.048.

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Support Information for "*In situ* Measurement of Solution Concentrations and Fluxes of Sulfonamides and Trimethoprim Antibiotics in Soils Using o-DGT"

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Figure S1 Masses of antibiotics accumulated by o-DGT versus deployment time (regression: polynomial, order 2).

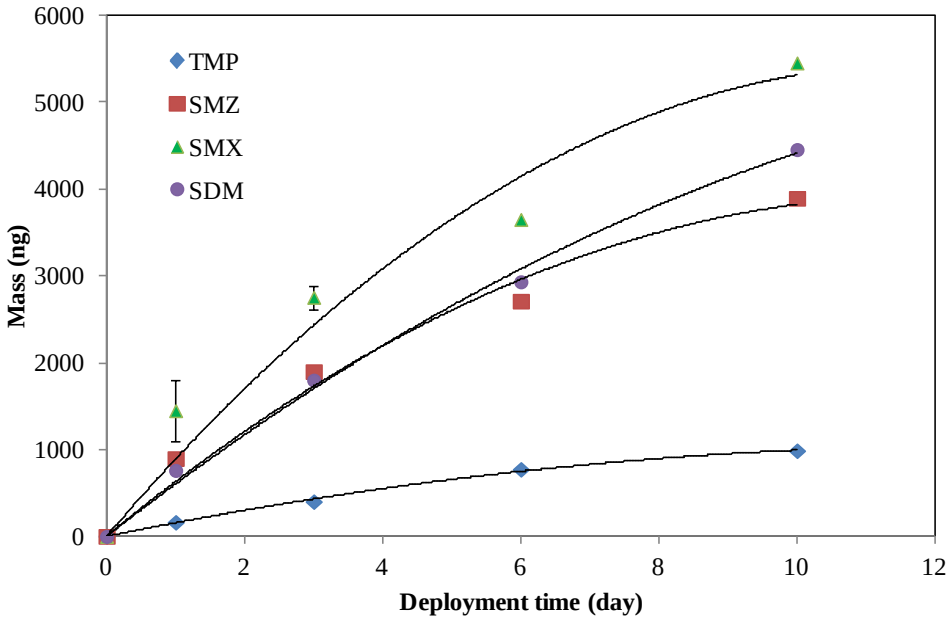

Figure S2. Deployment of o-DGT devices in soils (left) and disassembled o-DGT devices after deployment (right)

Table S1 Concentrations (ng/mL) of 4 antibiotics in the soil solution at different time after spiking (mean (sd), n = 3).

Time (day)	1	2	4	7	10	15	19
TMP	21.8(0.6)	19.2(1.7)	16.4(2.4)	14.1(1.8)	13.3(0.6)	13.1(2.1)	12.6 (3.5)
SMZ	241(13.6)	196(11.8)	184(13.7)	116(2.1)	118(4.3)	116(19.1)	122(4.4)
SMX	437(18.4)	376(10.2)	408(26.9)	291(16.1)	298(9.0)	307(64.2)	303(10.8)
SDM	152(10.3)	120(14.6)	130(9.7)	100(2.9)	96.3(5.6)	101(22.6)	98.4(3.0)

Appendix II

Abstract for *23rd SETAC Europe Meeting* in Glasgow, UK, 2013:

A Passive Sampler for *in situ* Measurement of Pharmaceutical and Personal Care Ingredients in Waters

Fisheries and Protection of Waters, South Bohemian Research Center of Aquaculture and Biodiversity of Hydrocenoses. Pharmaceuticals and personal care products (PPCPs) are introduced to the water environment by anthropogenic inputs, being only partially metabolized by human body. Such compounds are not effectively removed by waste water treatment plants (WWTP). Therefore, PPCPs are detected in WWTP effluent, consequently reaching surface waters. Among the sampling methods, spot sampling is the most frequently used one. The main disadvantage is that the information obtained from the sample is unique to the place and the time selected. To obtain more representative data automatic samplers can be used. Another option is passive sampling, which is less sensitive to accidental variations of the pollutant concentration and gives time-weighted average (TWA) concentrations. The application of two different approaches for the monitoring of waste water pollution was evaluated. Content of 130 PPCPs was measured in both time proportional pooled water samples taken by automated sampler and extracts from 2 configurations of POCIS samplers. Passive sampling was advantageous regarding the limits of detection: more than 50 PPCPs were detected only in POCIS extracts but not in pooled water samples. One of the probable reasons for that could be loss of target analytes during the storage. In case of waste water, storage and preservation of the sample could be of great importance in order to get data that will reflect the real situation. Storage at higher temperatures can enhance bacterial growth in solution, resulting in losses of target analytes. Different regimes of storage were tested: fridge (+4

TH069 A Passive Sampler for in situ Measurement of Pharmaceutical and Personal Care Ingredients in Water W. Chen, C. Chen, H. Zhang, K.C. Jones, Lancaster University / Lancaster Environment Centre; O.R. Price, Unilever / Safety and Environmental Assurance Centre; G. Ying, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences; N. Xu, Peking University Shenzhen Graduate School / School of Environment and Energy; H. Li, A.J. Sweetman, Lancaster University / Lancaster Environment Centre. Pharmaceutical and personal care products (PPCPs) contain a diverse group of emerging chemicals which have generated interest with both scientists and the public. As a result of their high consumption rates and continuous release into aquatic environments, they can achieve relatively steady state concentrations in the environment. However, the environmental fate and effects of these chemicals are poorly understood, in particular the bioavailable fraction and risks these chemicals may pose to aquatic organisms and humans via environmental exposure. A novel passive water sampler based on the theory of the diffusive gradients in thin films (DGT) has been developed for *in situ* sampling for a subset of chemicals, particularly, parabens, phenols and estrogens. The sampler provides a quantitative and time-integrated measurement of chemical concentration in aqueous systems without field calibration. Laboratory testing and performance characteristics of organic-DGT (o-DGT) have been carried out, with methylparaben (MeP), propylparaben (PrP) isopropylparaben (iPrP), ortho-phenylphenol (OPP), butylated hydroxyanisole (BHA), bisphenol-A (BPA), estrone (E1), ?-estradiol (E2), estriol (E3), 17?-ethinylestradiol (EE2) and triclosan (TCS) as model compounds. The capacity of three types of binding resins (XAD18, HLB and SXA) have been tested and compared. Agarose gel (AG) was selected as the most suitable diffusive layer as it did not significantly adsorb the test substances. Uptake of chemicals by o-DGT increased with exposure time and with the inverse of diffusive layer thickness (0.25mm-2mm). o-DGT performance under different conditions, such as pH (4-9), ionic strength (0.001M-0.5M) and organic matter (0-8mg/L), has also been evaluated. *In situ* field measurements have been compared to grab samples collected in natural waters and wastewaters to determine the potential application of these novel passive samplers.

TH070 Laboratory calibration of the POCIS and application to the passive sampling of 40 pesticides in rivers of an agricultural watershed in south of France g. poulier, Irstea / Unité de recherche REBX; C. Adeline, S. Lissalde, R. Buzier, P. fondaneche, E. Renaudie, Université de Limoges / Groupement de recherche eau sol environnement; N. Mazzella, Irstea / Unité de recherche REBX; G. Guibaud, Université de Limoges / Groupement de recherche eau sol environnement; F. Delmas, F. Delmas, B. Delest, A. Moreira, G. Jan, S. Moreira, Irstea / Unité de recherche REBX. Pesticides have been widely used in agriculture since the 1950s to improve productivity. However, a part of these compounds is often driven to water bodies via hydrological processes such as runoff, leading to a large and diffuse contamination of aquatic environments, with possible toxic effects to biota. During the last decades there has been an increasing concern about the fate of pesticides in water bodies, as shown by the implementation of the European Water Framework directive (2000/60/CE). This legislation involves an efficient monitoring of water quality, what is not yet possible with conventional methods like analysis of grab samples, due to low sampling frequency and inadequate limits of detection for some priority compounds. An answer could be the use of passive sampling devices like the polar organic chemical integrative sampler (POCIS). POCIS has been proven to be a very useful tool for screening, but a laboratory calibration step is necessary when quantitative data like time weighted average concentrations are needed. In our study we calibrated POCIS for 32 pesticides and 8 metabolites, commonly encountered in rivers. After this calibration step, several triplicates of POCIS have been successively exposed in three different rivers of an agricultural watershed in the south-west of France, over a period of 6 months (from March to September 2012). We observed high levels of metolachlore, an herbicide widely used for the treatment of corn and sunflower crops. Spring was identified as the most hazardous period for water quality, probably because of the succession of herbicides treatments and intense runoff after huge rain events. POCIS was able to integrate short variations of compounds concentrations, even for unexpected events like spates. In some cases we were also able to deduce the geographical origin of a contamination thanks to an adequate repartition of our POCIS on the watershed.

TH071 POCIS Calibration for pesticide monitoring : from lab to in-situ experiments a. togola, BRGM / Laboratory Division; I. Ibrahim, BRGM / Ecole des Mines d'Ales; C. Gonzalez, Ecole des Mines d'Alès. In order to estimate the water concentrations of pollutants from accumulated amounts in the sampler, laboratory or in situ calibration data are required in order to estimate the sampling rate (Rs) for each compound. The sampling rate of passive samplers depends on the physicochemical properties of the chemicals and the environmental conditions, such as temperature, water flow rate/turbulences and dissolved organic carbon. The challenge is to obtain TWA concentrations which are sufficiently representative of the real pollution levels in the aquatic medium. This goal is mainly dependent on the calibration of the passive sampler, generally conducted under controlled conditions at laboratory scale. However, as field environment is very different from laboratory conditions, use of inappropriate laboratory derived sampling rates for calculating TWA concentrations from passive samplers exposed in situ could lead to an inaccurate result of the real pollution levels. The aims of the present work were to study the uptake kinetics in surface water of a range of polar pesticides and metabolites by pharmaceutical POCIS samplers in order to determine sampling rates by in-situ calibration, to compare results with those obtained under laboratory conditions in order to assess the impact of environmental conditions on POCIS field performances. Finally, the objective is to evaluate the effectiveness of POCIS to determine TWA concentrations in the aquatic medium in comparison with the classical spot sampling methodology. The in situ experiment was conducted with samplers deployed in channel pilot system, an artificial irrigation canal bringing water from the Rhône River. Beside the numerous targeted pesticides, 13 compounds were detected in water samples including triazines, phenylureas, conazoles, chloroacetanilides, phenylamides and triazines metabolites , allowing the comparison between lab and *in situ* experiments. Accumulation during the 15 days exposure is linear for all compounds except DIA. For most of the compounds, the in-situ sampling rates were significantly lower by a factor of 3-5 than those from laboratory experiment, considering that field measured water velocity was 4 time lower than laboratory, the main effect of flow

Appendix III

Abstract for *Conference on DGT and the Environment* in Lancaster, UK, 2013:

Performance Comparison on Three Resins of o-DGT for *in-situ* PPCP Measurement in Waters

PERFORMANCE COMPARISON ON THREE RESINS OF O-DGT FOR *IN-SITU* PPCP MEASUREMENT IN WATERS

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The technique of diffusive gradients in thin-films (DGT) can provide quantitative *in-situ* measurements of trace components in aqueous systems. This popular passive sampler has been widely used throughout the world for monitoring inorganic components. Recently, the principles of DGT were successfully applied to the measurement of organic contaminants (o-DGT) using antibiotics as model chemicals (1).

To extend the application to the measurement of pharmaceutical and personal care products (PPCPs) in waters, three kinds of resins, XAD18, HLB and Strata-XL-A (SXA) were used as binding layers for developing o-DGT, with methylparaben (MeP), propylparaben (PrP) isopropylparaben (iPrP), ortho-phenylphenol (OPP), butylated hydroxyanisole (BHA), bisphenol-A (BPA), estrone (E1), β-estradiol (E2), estriol (E3) and 17α-ethinylestradiol (EE2) as model compounds.

Systematic laboratory testing evaluated the performance of o-DGT under different conditions. The investigation of uptake capacity of the device showed that all three resin gels can linearly take up PPCPs at a relative low concentration (about 2 mg/l), which is still much higher than environmental concentrations, and have similar uptake rates. For most chemicals, XAD18 has the largest uptake capacity, similar to HLB, while SXA has the smallest uptake capacity. Performance tests of o-DGT at various pH and ionic strengths (IS) showed that pH has little effect, while high IS (0.5M) significantly affected the measurement, indicating that o-DGT may not be suitable for analysis in seawater, unless it is calibrated specifically for ionic strength. Mass accumulated by all three o-DGTs increased linearly with the deployment time for most chemicals. The slope for the HLB-o-DGT plot agreed well with the theoretical prediction, demonstrating that HLB-o-DGT can be used for accurate measurements in aquatic systems. o-DGT equipped with XAD18 or SXA as the binding layer accumulated less mass (comparing to the theoretical prediction) and may not suitable for monitoring unless "effective" diffusion coefficients are used. HLB-o-DGT has been selected for field application to test its performance and suitability for in situ measurements under different environmental conditions.

(1) Chen, C, Zhang, H and Jones, K C. (2012). A novel passive water sampler for *in situ* sampling of antibiotics. *J. Environ. Monit.*, 14, 1523-1530.

POSTER

Appendix IV

Abstract for *DGT Conference 2015* in San Sebastián, Span:

Field Evaluation of o-DGT for *in situ* Measurement of Pharmaceuticals and Personal Care Ingredients in Wastewater

28th September to 1st October · Donostia-San Sebastián (Spain)
DGTConference2015
"From DGT Research to Environmental Assessment"

ABSTRACT for DGT CONFERENCE 2015

To be sent to meritxel.gonzalez@azti.es before 30th March 2015

FIELD EVALUATION OF O-DGT FOR *IN SITU* MEASUREMENT OF PHARMACEUTICAL AND PERSONAL CARE INGREDIENTS IN WASTEWATERS

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ABSTRACT

To evaluate the applicability of o-DGT under field conditions for the measurement of ingredients of pharmaceuticals and personal care products, HLB-o-DGT devices were deployed *in situ* at a wastewater treatment plant (WWTP) in the UK for 2 weeks and compared with active sampling approaches (both grab-samples and auto-samplers). All 11 target chemicals, except IPRP[1], were detected in the influent, for both active and passive sampling; while only 9 of 11 chemicals (except IPRP and PRP) were found in the effluent. For most of the detected chemicals, the mass accumulated into the o-DGT increased linearly with deployment time for 14 days in both the effluent and influent and confirmed the o-DGT is capable for field water sampling application and can provide quantitative measurements of pharmaceuticals and personal care products.

The 14-day time-weighted average (TWA) concentrations of detected chemicals measured by o-DGT were calculated and compared with the average concentration of active samples. It was noticed that, o-DGT TWA-concentrations were generally different from the results of active samples. One possible reason could be that o-DGT accumulated only the dissolved labile fraction of compounds, but grab/auto samples also contained some particulate fraction although filtered (0.7 μm) which led to higher concentrations. The lack of representative grab/auto samples could be another reason for the differences between the two sampling methods, while o-DGT accumulated target compounds throughout the period, measuring a TWA-concentration.

Reference:
1. Wei Chen, et al. A Passive Sampler for in situ Measurement of Pharmaceutical and Personal Care Ingredients in Waters. 23rd Annual Meeting of SETAC Europe, Glasgow, UK. May 12-16, 2013

KEY WORDS: o-DGT, Pharmaceutical and personal care products, Wastewater

TO BE PRESENTED IN **SESSION 1: Water solutions and aquatic environments**

ORAL or POSTER COMMUNICATION: **POSTER**