In situ monitoring method development for organophosphorus flame retardants in waters using the DGT technique

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Abstract

Widespread use of organophosphorus flame retardants (OPFRs) and their ubiquity in waters results in the need for a robust and reliable monitoring technique to better understand their fate and environmental impact. *In situ* passive sampling using the diffusive gradients in thin-films (DGT) technique provides time-integrated data and is developed for measuring OPFRs here. Ultrasonic extraction of binding gels in methanol provided reliable recoveries for all tested OPFRs. Diffusion coefficients of TCEP, TCPP, TDCPP, TPrP, TBP, TBEP and TPhP in the agarose diffusive gel (25 ºC) were obtained. The capacity of an HLB binding gel for OPFRs was >130 μg per disc and the binding performance did not deteriorate with time up to 131 d. DGT performance is independent of typical environmental ranges of pH (3.12–9.71), ionic strength (0.1–500 mmol L^{-1}) and dissolved organic matter (0–20 mg L^{-1}), and also of diffusive layer thickness (0.64–2.14 mm), and deployment time (3–168 h). Negligible competition effects between OPFRs was found. DGT-measured concentrations of OPFRs in a wastewater treatment plant (WWTP) effluent (12–16 d) were comparable to those obtained by grab sampling, further verifying DGT's reliability for measuring OPFRs in waters.

Introduction

Organophosphorus flame-retardants (OPFRs) are emerging contaminants which have been widely utilized in polyurethane foam plastic, resin, paint, textiles and building materials.[1] OPFRs are relatively water-soluble organic contaminants and physically added, rather than chemically bonded, to various materials. They can therefore easily transfer to environmental media, particularly to water. However, some OPFRs, such as chlorinated compounds tris(2-chloroethyl) phosphate (TCEP), tris(2-chloroisopropyl) phosphate (TCPP), and tris(1,3-dichloro-2-propyl) phosphate (TDCPP) cannot be effectively removed from wastewaters by activated sludge treatment and are quite recalcitrant to advanced oxidation process.[2] OPFRs may therefore be discharged to the environment through effluent and sludge. OPFRs are then ubiquitous in surface water, and have even been reported in tap water and bottled drinking water in many countries, including United Kingdom, Germany, Italy, America, and China.[3-7]. Tris(2-butoxyethyl) phosphate (TBEP) and TCEP are the most prominent OPFR compounds in some aquatic systems.[8,9] Total concentrations of OPFRs have been reported from 85 ng L^{-1} to 325 ng L^{-1} in tap water and up to 1660 ng L^{-1} in drinking water.[4,10]. The most frequently detected compounds in tap water were TBEP, triphenyl phosphate (TPhP), and TCPP and TCEP, TCPP and TBEP in bottled drinking water.

OPFRs may have adverse effects on ecosystem and human health. TCEP, TCPP, TPhP, tri-n-butyl phosphate (TBP), and TBEP can be bioaccumulated in fish and be transferred through the aquatic food web.[11-14]. Concerns over human exposure to OPFRs has focused on endocrine disruption via disturbing steroidogenesis,[15] inducing oxidative stress,[16] or influencing thyroxine.[17] Hence, accurate measurement and monitoring of OPFRs in aquatic systems is necessary to better understand their fate and biogeochemical behavior and to further evaluate their potential effect on ecosystems

and human health.

Usually OPFRs monitoring is by actively collecting large-volume water samples followed by preconcentration using solid-phase extraction. However, this only provides snapshots of OPFR concentrations at a certain sampling time. [4-6,10] The sample treatment is time-consuming and costly. The measurements cannot reflect any daily or weekly concentration fluctuations.[18] Passive sampling techniques, which preconcentrate analytes from water to binding agents *in situ* during field deployment, can overcome these drawbacks [18] and provide time-averaged concentrations, which better reflect environmental contamination levels and contribute to a more accurate risk assessment of ecosystems and human health. The polar organic chemical integrative sampler (POCIS) has been applied to monitoring organic contaminants, including organophosphate pesticides and EDCs, in waters.[19,20] However, a significant limitation of POCIS is that its sampling rates largely depend on hydrodynamic conditions. Calibration carried out in the laboratory cannot reflect the *in situ* conditions.

The diffusive gradients in thin-films (DGT) technique is independent of hydrodynamic conditions and hence no calibration is needed for *in situ* measurements.[21](The principles of the DGT technique are given in the Supporting Information, SI). DGT is well established for measuring various inorganic species in aquatic systems.[21-29] Recently DGT has been extended to measuring organic pollutants, such as antibiotics,[30,31] bisphenols,[32] pesticides,[33] house-hold and personal care products (HPCPs),[34] and some polar chemicals in waste water treatment plants.[35] These developments have made it feasible to use DGT for measuring OPFRs in waters.

HLB (Hydrophilic-lipophilic-balanced) resin (N-vinyl pyrrolidone and divinyl benzene copolymer) has been widely used in cartridges to extract polar organics, including OPFRs.[4,6] Here DGT devices containing HLB resin incorporated in agarose

gel as binding phase were prepared to effectively sample seven frequently detected or studied OPFRs, i.e., TCEP, TCPP, TDCPP, TPrP, TBP, TBEP, and TPhP for the first time. DGT was evaluated for its performance characteristics under various pH, ionic strength, and dissolved organic matter concentrations which cover the range typically found in the environment. The possible effects of binding kinetics, capacity of the binding gels, deployment time, competition among different OPFRs, storage time of the HLB binding gels, and diffusive gel thickness were also studied. DGT was deployed in wastewater treatment plant effluent in Nanjing, China to evaluate its performance in field conditions.

Method and Materials

Gel preparation. A standard DGT device consists of a binding gel, a diffusive gel and a filter membrane held in a plastic molding (DGT Research Ltd, UK).[32] Diffusive gels were prepared using agarose solution following previously published procedures.[31,32] Information on the evaluation of possible adsorption of OPFRs onto filter membranes, diffusive gels and DGT moldings is given in the parts of Method and Materials and Results and Discussion of the SI.

Binding gels were prepared by adding 3.6g (wet weight) of HLB resins into 18 mL of 2% agarose solution (dissolving 0.36 g of agarose in 18 mL of MQ water) when the solution was heated to transparent. The resulting solution was then pipetted into pre-heated glass plates separated by a 0.50 mm thick PTFE spacer. The diffusive gels were made following the same procedure without the resin. When gels were set at room temperature they were then cut into discs of 2.5 cm diameter and stored in 0.01 M NaCl solution at 4 °C.

106 **Uptake kinetics and elution efficiencies of HLB gels.** Preparation of reagents,
107 materials, and solutions used in the following sections are detailed in the SI. HLB gel
108 discs were immersed in 10 mL of 100 μg L^{-1} OPFRs solutions and shaken horizontally
109 for various times, from 0.5 min to 24 h. The masses of OPFRs adsorbed by the HLB
110 gel discs was calculated by the difference between the original concentration and the
111 remainder in each sample.

112 Elution efficiencies of OPFRs were assessed by eluting HLB gels pre-loaded with
113 various amounts of OPFRs with 10 mL of methanol. Hence, HLB gels were immersed
114 in 10 mL of 10, 20, 50, 100, and 200 μg L^{-1} OPFRs solutions containing 0.01 M NaCl,
115 and shaken horizontally for 24h. The OPFRs-loaded HLB gels were extracted using 10
116 mL of methanol in an ultrasonic bath for 30min. The elution and immersion solutions
117 was then filtered using PTFE filter membranes with 0.22 μm pore size and analyzed
118 using UPLC–MS/MS.

119 **Diffusion coefficients.** Diffusion coefficients of OPFRs were measured following
120 a previously widely described method, but with a slight modification.[24,26,36] In brief,
121 they were measured with two stainless steel compartments connected with a 1.5cm
122 diameter circle window holding a 0.75 mm thick diffusive gel. The source compartment
123 was filled with 50 mL of 0.01 M NaCl solution containing 1 mg • L^{-1} OPFRs, while the
124 receptor compartment contained 50 mL of 0.01 M NaCl solution without any OPFRs.
125 The solution pH in both compartments was the same (5.91 ±0.23). An aliquot of 0.2 mL
126 was removed to glass vials, for further instrumental analysis, from both compartments
127 at intervals of 30 min each time. The experiments were performed at 22.1±0.2°C for

270 minutes. Diffusion coefficients, D_{cell}, measured in this way were calculated using equation 1:

$$D_{cell}=slope\frac{\Delta g}{CA} \quad (1)$$

Where Δg is the thickness of agarose diffusive gel, C means concentrations of OPFRs in the source compartment, and A represents the area of the window connecting the two compartments. The slope was obtained by plotting the diffused masses of OPFRs versus diffusion time.

Diffusion coefficients, D_{DGT}, of OPFRs were also measured by deploying 8 DGT devices in 2.5 L of 20 μg L^{-1} well-stirred OPFRs solutions for 24 h, assuming DGT-measured concentrations of OPFRs were equal to solution concentrations. D_{DGT} was calculated using a previously reported equation:[32]

$$D_{DGT}=\frac{M\cdot\Delta g}{C\bullet A\bullet t} \quad (2)$$

Where M is the mass accumulated on the HLB binding gels, Δg is the thickness of the diffusive layer (a diffusive gel and a filter), C is the solution concentration of OPFRs, A is the area of exposure window of the DGT device (2.51 cm^2), and t is the deployment time.

DGT performance under different conditions. Standard DGT devices containing a 0.5 mm thick HLB binding gel, a 0.75 mm thick agarose diffusive gel, and a 0.14 mm thick, 0.45 μm pore size hydrophilic PTFE filter membrane were deployed in various OPFRs solutions for 24 h to evaluate the effects of pH, ionic strength, and

dissolved organic matter on DGT performance. The solutions were (a) 2.5 L of 20 μg L^{-1} OPFRs solutions containing 0.01 M NaCl with a range of pH from 3.1 to 9.5; (b) 2.5 L of 20 μg L^{-1} OPFRs solutions containing various NaCl concentrations ranging from 0.0001 to 0.5 M at pH 6; (c) 2.5 L of 20 μg L^{-1} OPFRs solutions (C_{NaCl} = 0.01 M, pH6) with a range of humic acid (Aladdin, fulvic acid ≥ 90%) concentrations, from 0 to 20 mg L^{-1}.

To test the effect of deployment time on DGT performance, the DGT devices were deployed in 6 L of 20 μg L^{-1} OPFRs solutions containing 0.01 M NaCl and retrieved at different time (from 3 h to 168 h). To explore the dependence of mass taken up by DGT on diffusive gel thicknesses, DGT devices with various thicknesses of agarose diffusive gels were immersed in 2.5 L of 20 μg L^{-1} OPFRs solutions containing 0.01 M NaCl for 24 h.

Capacity and competition effect. To measure the capacity of DGT to accumulate OPFRs, the DGT devices were deployed in 2.5 L of well-stirred solutions containing 0.01 M NaCl with OPFRs concentrations ranging from 20 to 1800 μg L^{-1} for 24h.

To investigate potential competition effect among OPFRs, seven studied OPFRs were divided into 3 groups: alkyl OPFRs (TBP, TBEP, and TPrP), aryl OPFRs (TPhP), and chlorinated alkyl OPFRs (TCEP, TCPP, and TDCPP). DGT devices were immersed in various mixed solutions: (a) alkyl OPFRs were at 20 μg L^{-1}, while the others were at 100 or 1000 μg L^{-1} respectively; (b) aryl OPFRs were at 20 μg L^{-1}, while the others were at 100 or 1000 μg L^{-1} respectively; (c) chlorinated alkyl OPFRs were at 20 μg L^{-1}, while the others were at 100 or 1000 μg L^{-1}, respectively.

DGT tests *in situ* in field trials. To further test the robustness of DGT for measuring OPFRs in the real environment, the devices were applied to monitor concentrations of OPFRs in a wastewater treatment plant (WWTP) for sewage with anaerobic-anoxic-oxic (A^2/O) treatment process in Nanjing. The WWTP mainly treats domestic wastewater. The capacity of sewage treatment is about 100,000 m^3 d^{-1}. The DGT deployments were carried out for 12–16 days. Six DGT devices were assembled into hexahedral units to allow each DGT device the same chance to accumulate OPFRs from water.[24,32] A temperature button data logger was set with each hexahedral unit to record the water temperature every 180 minutes. On retrieval, DGT devices were immediately transported to the laboratory, HLB binding gels were eluted with 10 mL methanol in an ultrasonic bath for 30 minutes. Water samples (0.5 L) were collected from each sampling site every 2–3 days during DGT deployment and concentrated with HLB cartridges (Waters, 6 cc 150 mg), followed by elution twice with 5 mL of methanol. The two eluents were merged. Both HLB binding gel eluents and cartridge eluents were evaporated to near dryness under a gentle stream of nitrogen, and then re-dissolved with 0.5 mL of methanol for further instrumental analysis.

Results and Discussion

Uptake kinetics of OPFRs onto HLB gels. Accumulated OPFRs on HLB binding gels increased almost linearly with time in the first 30 minutes. More than 80% of OPFRs were bound onto the HLB gels after 60 minutes (Figure 1, Figure S3). The

194 average binding rates of the analytes over the first 30 minutes were 2.42, 2.20, 2.02,
195 2.06, 1.79, 1.55 and 2.14 ng min^{-1} cm^{-2} for TCEP, TCPP, TDCPP, TPrP, TBP, TBEP and
196 TPhP, respectively. They were much higher than those calculated from DGT devices
197 deployed in 200 μg L^{-1} OPFRs solutions for 24 h at 24 ºC (1.02, 0.70, 0.73, 0.86, 0.74,
198 0.66, and 0.56 ng min^{-1} cm^{-2} for TCEP, TCPP, TDCPP, TPrP, TBP, TBEP and TPhP
199 respectively). It suggests HLB gels can adsorb OPFRs rapidly enough to ensure OPFRs
200 concentration at the interface between the diffusive gel and HLB binding gel is
201 effectively zero, which is a requirement for the DGT technique.[21]

202 **Elution efficiencies of OPFRs loaded on HLB gels.** Reliable elution efficiencies
203 of OPFRs are required for accurate calculation of DGT-measured concentrations using
204 eq. S1. Consistent and stable elution efficiencies of 100% were obtained for the OPFRs
205 using 10 mL of methanol across a series of exposure concentrations (10-200 μg L^{-1}) by
206 extraction in an ultrasonic bath for 30 min (Table S3). High elution efficiencies here are
207 consistent with XAD 18 binding gels for antibiotics [30] and MIP binding gels for 4-
208 chlorophenol[37]. They are also comparable to HLB binding gels for HPCPs [34] and
209 pesticides [33], but higher than AC binding gels for bisphenols (52–62%) [32] and MAX
210 binding gels for pesticides (46–86%) [33].

211 **DGT blanks and method quantitation limits.** Table 1 summarizes DGT blank
212 concentrations, instrument quantitation limits (IQLs) and DGT method quantitation
213 limits (MQLs) of OPFRs. DGT blank concentrations of OPFRs were achieved by
214 measuring the mass of the analytes on HLB binding gels retrieved from DGT devices
215 which were assembled and left for 24h without deployment. Table 1 shows that 5 of the

studied OPFRs were detected in the HLB gels with quite low concentrations (0.01–0.22 ng per disc), with a little higher detection of TCEP and TBP (0.75 ± 0.32 and 1.51 ± 0.34 ng per disc). IQL was defined as the lowest point on the calibration curve which could be accurately measured within ±20% of its nominal value. MQLs were calculated from IQL, assuming a DGT device with a 0.75 mm thick diffusive gel and a 0.14 mm thick filter membrane was deployed for 14 days at 25 ºC. MQLs ranged from 0.25 to 0.32 ng L^{-1} for the studied OPFRs (Table 1). OPFRs in fresh water were 7.3–96 ng L^{-1} in the North American Great Lakes [9], 0.6–0.8 μg L^{-1} in the River Tiber (Italy) [3] and ~1 μg L^{-1} in the Songhua River, China [8]. In WWTPs, reported concentrations of OPFRs were 3.67–150 μg L^{-1} in Spain,[2] 3.3–16.3 μg L^{-1} in Germany,[6] and 0.8–1.4 μg L^{-1} in China.[38] Given the much lower values of the MQLs for OPFRs than reported concentrations in surface water and WWTPs, DGT coupled with UPLC-MS/MS have the required sensitivity for measurement of OPFRs in waters. If the concentrations of OPFRs in some samples were < MQLs, a longer deployment time or merging two or more HLB binding gels into one sample will improve the measurable mass and reduce the MQLs.

Measurement of diffusion coefficient. For use of the DGT method it is vital to accurately measure diffusion coefficients of targeted analytes. The measurements were carried out and god linear relationships (r^2 = 0.986–0.999) of diffused masses versus time were obtained (Figure S4) using diffusion cell device. D_{cell} was calculated using eq. 1 and calibrated to 25 °C using eq. 3[31]:

$$\log D_t = \frac{1.37023(t\text{-}25)+8.36\times10^{-4}(t\text{-}25)^2}{109+t} + \log\frac{D_{25}(273+t)}{298}$$

238 (3)

239 The D_{cell} diffusion coefficients at 25 °C were 5.87×10^{-6}, 5.56×10^{-6}, 5.11×10^{-6},
240 5.53×10^{-6}, 4.99×10^{-6}, 4.58×10^{-6} and 5.53×10^{-6} cm^2 s^{-1} for TCEP, TCPP, TDCPP,
241 TPrP, TBP, TBEP and TPhP, respectively. They are similar to the values of D_{DGT} (6.37
242 $\times10^{-6}$, 5.34×10^{-6}, 4.63×10^{-6}, 5.82×10^{-6}, 5.32×10^{-6}, 4.06×10^{-6} and 3.96×10^{-6} cm^2
243 s^{-1} for TCEP, TCPP, TDCPP, TPrP, TBP, TBEP and TPhP respectively) using DGT
244 devices in a well-stirred OPFRs solutions for 24h. The ratios of D_{cell} to D_{DGT} for most
245 selected OPFRs were in the range from 0.9–1.1. (Table S4) The only two exceptions
246 were TPhP and TBEP, the ratio of D_{cell} to D_{DGT} for which were 0.72 and 0.89,
247 respectively. Adsorption onto PTFE filter membranes on the DGT devices might
248 contribute to relatively lower D_{cell} /D_{DGT} for TPhP. When performing the experiments
249 of DGT capacity and time-dependence, it was found that longer deployment time in
250 water solutions could reduce the adverse effect on performance caused by the
251 adsorption onto PTFE filters. In this study, DGT-measured concentrations of TPhP and
252 TBEP became closer to theoretical values if DGTs were deployed for longer times in
253 solutions (Figure S8).

254 Previous studies demonstrated that diffusion coefficients of chemicals are
255 influenced by their octanol-water partition coefficient ((log K_{ow}) [31,36] The K_{ow} reflects
256 the hydrophilicity of analytes, which can influence the diffusion process through
257 diffusion layers. Thus, we further explored the relationship between D and log K_{ow}. A
258 good linear relationship (r^2 = 0.98) was obtained for chlorinated alkyl OPFRs (TCEP,
259 TCPP, and TDCPP) and two alkyl OPFRs (TPrP and TBP) (Figure 2), which have

similar chemical structures (Figure S1). This relationship may apply to the calculation of D for other OPFRs, which were not included in our study but have similar chemical structures. However, OPFRs with different structures, such as TBEP and TPhP, did not satisfy this equation.

DGT performance under different conditions. Solution pH could potentially influence adsorbent surface properties and the diffusion of the target analyte and thus affect the DGT measurement. However, changing solution pH (3.12–9.71) did not affect the DGT measurement of OPFRs with C_{DGT}/C_{soln} ranging from 0.85 to 1.09 (Figure 3). C_{DGT}/C_{soln} of TPhP was a little lower when pH >8, but no significant differences were observed among varying pH values (ANOVA, $p > 0.05$).

The effect of ionic strength (IS) on DGT performance for measuring OPFRs is demonstrated in Figure S5. The result indicates that most of the OPFRs studied were not significantly influenced by IS in solutions containing 0.0001-0.1 M NaCl, with most ratios of C_{DGT}/C_{soln} in the range of 0.9–1.1 (Figure S5). The only exception was for TPhP: almost all the ratios of C_{DGT}/C_{soln} were <0.90, but no significant differences were found among solutions containing varying concentrations of NaCl (0.0001–0.1 M) (ANOVA, $p > 0.05$). When IS concentration increased to 0.5 M, the ratios of C_{DGT}/C_{soln} for TCEP, TPrP and TBP remained in the range of 0.9–1.1, but for other tested chemicals were slightly lower than expected. A significant reduction in C_{DGT}/C_{soln} was observed for TPhP (ANOVA, $p > 0.05$). IS could potentially change the charge density and thus influence the diffusion process of tested chemicals.[23] TPhP, with three benzene rings, is more susceptible to charge density change. A similar phenomenon was

282 previously observed when XAD gels were used for illicit drugs and the possible reason
283 was the reduced hydrophilicity of tested chemicals at high IS.[39]

284 No significant effect of DOM on DGT measurement was observed in this study.
285 The ratios of C_{DGT}/C_{soln} for most of the tested OPFRs in solution containing 0–20 mg
286 L^{-1} DOM were between 0.9–1.12 (Figure S6). However, for TPhP, the ratios of
287 C_{DGT}/C_{soln} were lower than expected when DOM concentrations increased. DOM tends
288 to bind more hydrophobic organic compounds with higher log K_{ow}[40,41] (log K_{ow} for
289 TPhP is 4.59, Table S1), resulting in bound analytes with larger chemical structures
290 which are difficult to pass through the diffusion layer. Similar phenomena were
291 observed in Chen et al.'s[34] study on DGT performance for TCS and Dong et al.'s[37]
292 study on DGT performance for 4-CP, where the ratios of C_{DGT}/C_{soln} of TCS and 4-CP
293 decreased when DOM concentration increased. Our study indicates that DGT is an
294 effective tool for measuring OPFRs under typical environmental conditions covering a
295 wide range of pH, IS and DOM with the exception of TPhP.

296 **Effect of diffusive gel thickness and deployment time.** Adsorbed masses of
297 OPFRs by DGT containing diffusive gels of different thickness correlated with the
298 reciprocal of the thickness (0.64–2.14 mm) of the diffusive layers (Figure S7). This
299 demonstrated the accuracy of D_{cell} measured in this paper and further implied that DBL
300 thickness rarely affected the DGT measurements in the case of well stirred solutions.

301 Long-time deployment always occurs when monitoring trace pollutants, especially
302 organic pollutants due to low concentrations in waters.[31,32,34,39] The robustness and
303 reliability of DGT in long-time deployment is vital. DGT-measured masses of OPFRs

had a linear correlation with the increasing deployment time (3–168 h) and fitted well with the theoretical lines calculated from the known concentrations of deployment solutions using eq. S1 (Figure S8). The results are in accordance with Chen et al.'s study on HPCPs with DGT device containing HLB gels, where the accumulated masses of HPCPs increased linearly with increasing deployment time over 120 h.[34]

Binding capacity and competition among OPFRs. Enough capacity is critical for deployments of long-time or in heavily polluted areas. Accumulated masses of OPFRs measured by DGT linearly increased with their increasing solution concentrations. As shown in Figure 4, DGT devices can simultaneously accumulate 25.5, 25.0, 19.9, 18.8, 12.9, 11.9 and 16.3 μg of TCEP, TCPP, TDCPP, TPrP, TBP, TBEP and TPhP, respectively when the deployment solution concentrations reached around 1800 μg L^{-1}. The capacity of HLB gels for binding OPFRs is much higher than 130 μg per disc, which is comparable to that of XAD 18 gels for antibiotics (0.18 mg per disc)[30] and AC gels for bisphenols (140-194 μg per disc)[32]. The total capacity for OPFRs here is higher than reported capacities of HLB gels and MAX gels for anionic pesticides (52 and 50 μg per disc for HLB gel and MAX gel, respectively) prepared by Guibal et al., [33].he maximum effective capacities in this study was not reached. Providing the concentration of OPFRs at deployment sites is 10 μg L^{-1}, DGT could theoretically be deployed for about 3 years. When the concentration of OPFRs is up to 100 μg L^{-1}, DGT can work for over 3 months. Reported concentrations of OPFRs were usually at ng L^{-1} levels in surface waters[3,8,9] and from ng L^{-1} to several μg L^{-1} level in WWTPs[6,7,38]. Therefore, the measured binding capacities of DGT devices are enough for monitoring

OPFRs in aquatic system.

DGT devices were deployed in a series of synthetic solutions with different concentration ratios (20–1000 μg L^{-1}) of OPFRs to evaluate whether they would interfere each other through competitive binding. Table S5 lists the C_{DGT}/C_{soln} values of the studied OPFRs in solutions containing different concentration ratios of OPFRs. No evident interferences among tested chemicals were found, indicating potential competition effects between OPFRs are probably negligible for conditions tested.

Field Trial at a WWTP effluent. For field deployment, the storage of the DGT devices was investigated for up to 131 days. DGT performance was not affected by the storage time (Table S6). To verify DGT field performance, the devices were deployed *in situ* in the effluent of a WWTP in Nanjing, China for 12–16 days in this study (24 °C, pH 7.14). All tested chemicals, except TPrP, were detected in the effluent of the WWTP (Figure 5). Total OPFRs concentrations obtained by grab sampling during 12-day and 16-day deployment campaigns were 267.9 ± 31.2 and 265.4 ± 30.9 ng L^{-1}, respectively, indicating a relatively stable state of OPFRs concentrations in the effluent of the WWTP. The concentrations of OPFRs are much lower than those reported for other WWTPs, including WWTPs in Spain (μg L^{-1} level)[2], Sweden (7.9–39 μg L^{-1})[42], and Austria (several μg L^{-1})[43], but comparable to that in an industrial WWTP in Germany (397 ng L^{-1})[44]. Most of the maximum and minimum concentrations obtained by DGT method were within the maximum and minimum grab-sampling-measured values (Figure 5), demonstrating DGT is suitable for measuring OPFRs in effluents of WWTPs.

Conclusion and prospective. Grab sampling is widely used for monitoring organic contaminants due to its easy operation and good reproducibility. Since grab sampling only provides a snapshot of OPFRs at a certain sampling time and may miss or only capture the episodic concentrations of contaminants, such as point source or discharge events. Therefore, results obtained from grab sampling usually lack representativeness, especially under conditions with high variations in concentration. POCIS, which accumulates analytes transported from water to binding agents during *in situ* deployment, successfully overcomes these drawbacks and provides time-integrated data. Though POCIS has made certain achievements in monitoring organic contaminants, [20,45] its sampling rate is highly dependent on environmental conditions, such as water flow, which would reduce the accuracy and reliability of its results.

In this study, another passive sampler, DGT has been developed for monitoring OPFRs in waters. DGT is not susceptible to environmental conditions, thus can provide steady sampling rates. DGT is independent of pH (3.12–9.71), IS (0.1–500 mM) and DOM (0–20 mg L^{-1}). DGT-measured concentrations of OPFRs were consistent with those measured by grab sampling method in a WWTP effluent, indicating DGT is a robust and reliable tool for OPFRs monitoring in aquatic systems. DGT could be also used as an effective tool to evaluate OPFRs removal efficiency at different treatment process in WWTPs, although further investigation is still required.

■ ASSOCIATED CONTENT

Supporting Information

Detailed principles of DGT technique and detailed information on tested chemicals, analytical methods and QA/QC are provided. Detailed information on methods to check

potential adsorption onto materials and aging effect; Results and discussion on potential adsorption onto materials and aging effect; Tables and figures of potential adsorption onto materials, elution efficiencies, diffusion coefficients, uptake kinetics, effects of IS, DOM, diffusive gel thickness, deployment time, binding gel storage time, and competition binding are also provided.

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