Development and Applications of Novel DGT Passive Samplers for Measuring 12 Per- and Polyfluoroalkyl Substances in Natural Waters and Wastewaters

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ABSTRACT

Extensive and long-term use of per- and polyfluoroalkyl substances (PFASs) has caused their widespread distribution in aquatic systems. A new Diffusive Gradients in Thin-films (DGT) passive sampling method based on use of weak anion exchanger (WAX) binding layer is developed here for monitoring five perfluoroalkyl carboxylic acids (PFCAs), five perfluoroalkane sulfonic acids (PFSAs) and two PFASs (6:2 FTSA and GenX) in waters. Performance of WAX based DGTs was independent of environmental conditions, namely pH (3.03-8.96), ionic strength (1-500 mM), and DOM content (4-30 mg L^{-1}). Diffusion coefficients (*D*) of the 12 PFASs in the diffusive gels were measured, 9 for the first time. Linear correlations between *D* and perfluoroalkyl chain lengths (CF_2) were established to obtain *D* for congener chemicals with the similar functional group and structure. The binding capacity of the WAX-DGT sampler was at least 440 μg PFASs per sampler, sufficient for applications in waters across a wide range of conditions and PFASs concentrations. Successful applications of WAX based DGT samplers in a waste water treatment plant (WWTP) and three rivers has demonstrated that DGT is a powerful tool for monitoring, surveillance and research of these 12 PFASs in aquatic systems, and can be extended to wider suites of PFs in future.

INTRODUCTION

Per- and polyfluoroalkyl substances (PFASs) are synthetic chemicals with strong C-F bonds. They have been widely used in cosmetics, kitchenware coating, carpets, fire-fighting foams and industrial manufacture, owing to their high thermal stability, hydro- and oleo-phobic properties, and high surface activity, since they were first synthesized in the 1940s.[1, 2] The persistence, bioaccumulation potential, and long-range transport potential of PFASs have led to their occurrence in birds, fish, and mammals from sources.[3, 4] PFASs have been detected in human milk and blood and may cause a variety of health effects.[3-7] Many international organizations and countries have therefore restricted their use and production.[1] Perfluorooctane sulfonate (PFOS) and its precursors are included in the Stockholm Convention on Persistent Organic Pollutants (POPs) and assessments are under way to include perfluorooctanoic acid (PFOA) and its related precursors on the list too.[1, 2] PFASs can undergo long-range transport via rivers, oceans and the atmosphere[8, 9]. Water bodies are important for regional and global transport, while recent studies discuss global scale atmospheric transport of PFASs. See refs 8, 9 and Sha et al (10.1021/acs.est.0c03804) for recent reviews and discussions of processes. . Hence there is a need to develop reliable and cost-effective techniques to monitor them in aqueous discharges, rivers and marine systems.

The general term PFASs covers thousands of substances, including perfluoroalkyl acids (PFAAs) and their precursors. Among them, perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkane sulfonic acids (PFSAs) are widely distributed in the aquatic environment and have been restricted under national/regional/global regulatory or voluntary frameworks.[2] Some perfluoroether carboxylic acids (PFECAs), a branch of PFAAs, have been produced to replace traditional PFOA as fluoropolymer high-performance materials.[10] Their chemical structures are stable and difficult to be degraded by most water treatment processes, including flocculation precipitation, general and biological filtration, oxidation with chlorine or ozone, UV irradiation and low pressure membranes.[11] Therefore, they are frequently found in tap water, drinking water, effluent and sludge.[3, 12] Concentrations of PFASs in raw wastewater vary from ng L^{-1} to μg L^{-1} around the world.[13] Accurate monitoring of PFASs in waters is a prerequisite to obtain information on their sources, distribution, fate, transport pathways and precise assessment of risks.

Grab sampling is a widely used method for monitoring the concentration of PFASs in waters.[14-16] However, it can only represent the environmental instantaneous concentration (EIC) at the time of sampling. In addition, target analytes in grab samples may change during transportation and pretreatment due to possible adsorption and degradation. Moreover, the pretreatment is tedious and time-consuming, and requires high professional skills of technical personnel. The processes of filtration, solid-phase microextraction, elution and nitrogen-blowdown are time-consuming and are eliminated by using DGT. Passive sampling avoids many of the shortcomings mentioned above, owing to its *in situ* collection of target analytes.[16] It can also provide time weighted average concentrations (TWAC), reflecting the average concentration over the sampling period. For example, polyethylene (PE) passive samplers can be used to measure PFASs in groundwater[17] and WWTP[18]. Currently, the polar organic passive sampler (POCIS)[19-22] has been reported for the measurements of PFASs. The sampling rate of POCIS needs to be known accurately, in order to calculate concentrations of analytes of interest.[23] The sampling rate is a function of the water flow rate and temperature, so can vary widely in field conditions and it is difficult to obtain accurate sampling rates. [20, 21] Calibration experiments or performance reference compounds are needed in the field deployment of POCIS. However, it is still a challenge to obtain accurate sampling rates under changing water flow rate and temperatures with POCIS[24].

The diffusive gradients in thin-films (DGT) technique is an alternative and very well established passive sampler; it is based on Fick's first law of diffusion[25] and was originally invented for measuring inorganic substances in situ without field calibration.[26-32] DGT samplers can enrich the target analytes *in situ*, avoiding the potential errors caused by sample transportation and pretreatment of grab sampling. The measured data integrate exposure concentrations over the sampling time to provide a time-weighted average (TWA) concentration. No correction is required for the field sampling rate, because uptake is controlled by diffusion through a well-defined diffusive layer. This has made it very attractive as a sampler to deploy in aquatic systems for an ever-increasing array of analytes, including trace organic contaminants.

Recently, DGT samplers containing different binding layers based on Amberlite macroporous adsorbent resin (XAD18)[33-36], hydrophilic lipophilic balanced resin (HLB)[34, 37], active carbon[38], and mixed-mode cation exchange resin (MCX)[39] have been successfully used to measure organic pollutants, such as antibiotics,[33] pesticides,[40] psychiatric pharmaceuticals,[39] bisphenols,[38] phosphorous flame retardants,[37, 41] illegal drugs[36] and household and personal care products (HPCPs)[34]. Although Guan et al.[35] have developed a DGT method based on XAD18 as the binding layer to measure PFOA and PFOS in water, Wong et al.[42] used weak anion exchanger resin (WAX) as the binding layer to measure 6 common PFASs (perfluorobutanesulfonic acid (PFBS), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), and perfluorooctanesulfonic acid (PFOS)). Stroski et al.[43] measured four more PFASs (N-ethyl perfluorooctanesulfonamide (EtFOSA), N-ethyl perfluorooctanesulfonamide ethanol (EtFOSE), N-methyl perfluorooctanesulfonamide (MeFOSA), and N-methyl perfluorooctanesulfonamide ethanol (MeFOSE)) use HLB as the binding layer. A new DGT sampler which can measure more PFASs would be very useful and timely, because there is great interest in quantifying a wide array of PFASs, to monitor changing use patterns and transformation/degradation behaviour in the environment. In this study, we used a binding layer containing WAX resin which is more suitable for anionic compounds to measure a range of typical PFASs. This includes traditional long-chain PFASs that were widely used before, such as PFOA and PFOS, short-chain PFASs, such as PFBA (Perfluorobutanoic acid), PFPeA (Perfluoropentanoic acid), PFHxA (Prerfluorohexanoic acid), PFHpA (Perfluoroheptanoic acid), PFBS (Perfluorobutane sulfonate), PFPeS (Perfluoropentane sulfonate), PFHxS (Perfluorohexane sulfonate), PFHpS (Perfluoroheptane sulfonate) and novel PFASs, such as 6:2 FTSA (6:2 fluorotelomer sulfonic acid) and GenX (Hexafluoropropylene oxide dimer ammonium salt) which were used as substitutes for long-chain PFASs (Table 1). Nine of them (PFBA, PFPeA, PFHxA, PFHpA, PFPeS, PFHxS, PFHpS, 6:2 FTSA and GenX) have not been measured using DGT before. The masses of the 12 individual PFASs accumulated onto four different binding gels based on XAD18, HLB, WAX and MAX (mixed anion exchanger) resins were compared to select the suitable binding gels for the new DGT sampler. The performance characteristics of WAX based DGT were tested, including uptake kinetics, effects of pH, ionic strength, dissolved organic matter (DOM), deployment time, and possible competition effects. Diffusion coefficients (*D*) of the 12 PFASs in the diffusive gel layer were determined for the first time and relationships between *D* and molecular properties were established, which can be useful to predict values for other PFASs in future. The newly developed DGT samplers were then tested in the field, at a wastewater treatment plant (WWTP) in Suzhou and three sampling sites on major rivers in Nanjing, China.

EXPERIMENTAL SECTION

DGT Preparation. A standard DGT sampler is composed of a binding layer for uptake of target analytes, a diffusive gel layer allowing free diffusion of the analytes, a filter membrane to protect the gel layers from damage by particles in the environment, and a standard plastic molding (DGT Research Ltd., UK) for housing the gel layers and filter membrane.[44] A range of filter membranes were tested in this study. They were made of: nylon (NL) (Anpel, Scientific Instrument Co. Ltd, Shanghai, China), GH polypro (GHP) (Pall, USA), polyether sulfone (PES) (Pall, USA), hydrophilic polytetrafluoroethylene (PTFE) (Anpel Scientific Instrument Co. Ltd, Shanghai, China) and cellulose acetate (CA) (Anpel Scientific Instrument Co. Ltd, Shanghai, China), all with diameters of 25 mm and pore sizes of 0.45 μm. The filter membranes were immersed in pure methanol for 12 h and washed with Milli-Q water three times, prior to further use. Polyacrylamide diffusive gel layers were prepared using acrylamide and agarose-derived cross-linker (DGT Research Ltd., UK), following the procedure described in Zhang and Davison;[44] agarose diffusive gel layers using agarose solution according to the procedure of Chen et al.[33] were also used.

Four types of binding layers were prepared for the initial comparison and selection process. XAD18 and HLB binding layers were prepared following the published procedures.[37, 39] The WAX and MAX binding layers were prepared using an agarose-based method. Briefly, two acid-cleaned glass plates separated by a 0.5 mm thick spacer were preheated in an oven at ~70 °C. Agarose powder of 0.36 g was mixed with 18 mL MQ water. The agarose water mixture was heated until it looked transparent. WAX or MAX resin of 3.6 g was added into the solution immediately and heated to boiling; then the solution was injected between the preheated glass plates and left at room temperature to cool and solidify for ~50 min. The glass plates were then opened and the binding gel cut into circular discs with a diameter of 2.5 cm. Filter membranes, diffusive gel discs and binding gel discs were all stored separately in 0.01 mol L^{-1} sodium chloride solution in a 4 °C refrigerator for further use. The details of adsorption tests for different materials (gels, filters and mouldings), comparison of binding resins and aging test for resin gels are described in the SI. The details of chemical analysis and losses onto the filter materials are all in the SI. “Water Sample Extraction” for SPE in page S7 elaborated the pretreatment method of the grab samples. "Possible adsorption or release of PFASs by/from diffusive gels, filter membranes and DGT moldings materials." in page S8 and S10 explains that the losses onto the filter materials have no influence on DGT performance. "Chemical Analysis" and "Quality assurance and quality control" in page S8 and S9 introduced instrument analysis methods. Tables S5 (Optimized mass spectrum parameters of PFASs measured using UPLC-MS /MS, retention time and the internal standard of PFASs.), S6 (UPLC gradient program) and S7 (IQL, DGT blanks, MQL for DGT technique and spike recovery (%) of solid phase extraction (SPE)) is the detailed data

Elution Efficiencies and Uptake Kinetics. A stable elution efficiency is a key parameter for precise assessment of accumulated mass on the binding gels and DGT-measured concentrations. WAX and MAX binding gels were separately immersed in 10 mL of PFASs solutions with the concentration of 5, 10, 20, 50 and 100 μg L^{-1} containing 0.01 mol L^{-1} NaCl and shaken at 200 r min^{-1} at 25 °C for 24 h. Different concentrations should be tested to ensure the stability of elution efficiencies. NaCl is added to simulate the ionic strengths of natural waters. All experiment in this study were carried out in a laboratory with room temperature of 25± 0.5 °C. The PFASs adsorbed by WAX binding gels were eluted using 10 mL of 5 ‰ (v/v) ammonium hydroxide in methanol for 24 h, while the MAX binding gels were eluted using 10 mL of 1% (v/v) ammonium hydroxide in methanol for 24 h, followed by adjusting pH using 1% acetic acid (1% acetic acid: 1% ammonium hydroxide in methanol = 1:1, v/v). After filtration through a polypropylene (PP) filter, the concentrations of PFASs in the eluent were analyzed by UPLC-MS/MS (Qsight 210, PerkinElmer). Calculation of the elution efficiency is described in the Supporting Information (SI).

The uptake of the target analytes by the binding gel must be quick enough to keep the concentration of analytes effectively zero at the interface between the binding gel and the diffusive gel. This is the key requirement for accurate calculation of DGT-measured concentrations using DGT equation (1).[25]

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

Where M is the mass of the target analyte accumulated on the binding gel layer. Δg expresses the thickness of the diffusive layer, including the thickness of the filter membrane. D is the diffusion coefficient of the target analyte in the diffusive layer. A represents the area of the exposure window and t means the deployment time of the DGT sampler in waters.

WAX binding gels were immersed in 10 mL of 100 μg L^{-1} PFASs solution containing 0.01 mol L^{-1} NaCl and shaken at 200 r min^{-1}. An aliquot of 100 μL solution was taken for analysis at 1, 5, 10, 20, 30, 40, 60, 120, 180, 300, 480 and 1440 minutes. Control samples were obtained without binding gels to eliminate any possible influence of containers.

Diffusion Coefficients of PFASs. According to eq. 1, the diffusion coefficient, D, is an indispensable parameter for calculating C_{DGT}. Diffusion coefficients were measured using a method based on a diffusion cell device.[29, 35, 37, 45] It consists of two compartments connected through a small circular hole with a diameter of 1.5 cm. Both the source compartment and the receptor compartment were filled with 50 ml of 0.01

mol L^{-1} sodium chloride solution with the same pH (5.63 ± 0.17), but the source compartment contained 2.5 mg L^{-1} PFASs. A 0.75-mm thick (Δg), 2.51-cm diameter agarose gel disc was sandwiched between the holes of the two compartments. During the 2-h experiment, the solutions in both compartments were stirred continuously at 24.4 ± 0.4 °C. Subsamples (100 μL) were pipetted from both compartments every 10 mins for analysis. A plot of mass of target analytes in the receptor compartment versus the experiment time was obtained. The diffusion coefficients, D, were calculated according to eq. 2.

$$D = slope\ \frac{\Delta g}{CA} \qquad (2)$$

The slope is obtained from the linear part of the plot. Here, A is the area, 1.77 cm^2, of the small round hole in the diffusion cell device and C is the concentration of target analytes in the source compartment.

An alternative method for determination of D assumes that the DGT measured concentration is equal to the concentration of the target analytes in the deployment solution. According to the DGT theory the diffusion coefficients, D_{DGT}, can be derived from the DGT equation 1.

DGT Performance Characteristics under Different Conditions. DGT samplers containing WAX binding gels (WAX-DGT) were immersed in continuously stirred 2 L of 20 μg L^{-1} PFASs solutions with different pH, different ionic strength (IS), and different contents of dissolved organic matter (DOM) at 25°C for 24 h to test the performance characteristics of DGT under different conditions: (a) IS = 0.01 mol L^{-1} NaCl, DOM = 0 mg L^{-1}, pH ranging from 3 to 9; (b) IS ranging from 0.001 to 0.5 mol

L^{-1} NaCl, DOM = 0 mg L^{-1}, pH = 5.6 ± 0.3; (c) IS = 0.01 mol L^{-1} NaCl, DOM ranging from 0 to 30 mg L^{-1}, pH = 5.6 ± 0.3.

To verify the principle of DGT, the responses of the new DGT samplers to the deployment time and diffusion layer thickness were tested. For the time response study, DGT samplers were deployed in continuously stirred 6 L of 20 μg L^{-1} PFASs solution containing 0.01 mol L^{-1} NaCl at 25°C for 3-168 hours. For the response to diffusion layer thickness, samplers were prepared using diffusive layers (including filter membrane) with different thicknesses ranging from 0.64 to 2.14 mm and immersed in stirred 2 L of 20 μg L^{-1} PFASs solutions, containing 0.01 mol L^{-1} NaCl at 25°C for 24 h.

Binding Capacity and Competition Effect. *Binding Capacity*. DGT samplers containing WAX binding gel layers were placed in stirred 2 L of 0.01 mol L^{-1} NaCl solutions containing 10, 20, 50, 100, 200, 500, and 800 μg L^{-1} PFASs at 25°C for 72 h.

Competition Effect. The studied PFASs in this research can be divided into three categories, according to their chemical structures: PFCAs, PFSAs and two novel PFASs. Any competition on the uptake by DGT samplers may affect the DGT measurement and needs to be tested. DGT samplers were immersed in stirred 2 L of 0.01 mol L^{-1} NaCl solutions, containing different concentrations of the three categories at 25°C for 24 h: (a) Concentrations of PFCAs were 20 μg L^{-1}, PFSAs were 100 μg L^{-1}, while novel PFASs were 500 μg L^{-1}; (b) PFCAs were 100 μg L^{-1}, PFSAs were 500 μg L^{-1}, while novel PFASs were 20 μg L^{-1}; (c) PFCAs were 500 μg L^{-1}, PFSAs were 200 μg L^{-1}, while novel PFASs were 100 μg L^{-1}.

***In situ* application of DGT technology in the field.** In order to validate the robustness of the newly developed DGT samplers in the field, they were deployed in a wastewater treatment plant (WWTP) in Suzhou and three rivers in Nanjing (details are shown in Table S9). All DGT deployments and water sample collections were carried out between July and August 2019 in Nanjing and Suzhou, Jiangsu province. These sites are in the Yangtze River delta, one of the most economically and industrially developed regions in China.

The wastewater of the Suzhou WWTP is derived mainly from surrounding factories, including a photoelectric power plant, an electroplating plant and coating factory. The WWTP uses activated sludge processes for sewage treatment and treats ~8,000 tons of sewage every day. In addition, three sampling points in Nanjing located on the Qinhuai River (QH), Yunliang River (YN) and Yangtze River (YZ) were selected. Qinhuai River is the largest urban river in Nanjing and a tributary of the Yangtze River. Yunliang River is one of the tributaries to Qinghuai River. Six DGT samplers were assembled into a hexahedron, leaving the exposure windows of each DGT sampler facing outwards. At the same time, a button thermometer (Maxim Integrated Products, United States) was attached to each hexahedron to record the water temperature every 3 hours, to temperature-correct the compound-specific diffusion coefficients over the deployment period. Three DGT hexahedron units were deployed at the water inlet and outlet of the WWTP and three other units were deployed at three sampling points in the rivers for 12 days. Water samples were also collected at each sampling site (1 L volume) every two days and the water pH recorded. All water samples were extracted using a solid phase extraction (SPE) method as described in the SI.

RESULTS AND DISCUSSION

Adsorption test and Selection of DGT materials. The adsorption of PFASs on all the DGT components, except the binding gel, should be minimal to avoid any interference with the measurements. The test results (Figure S1) showed that the adsorption of all targeted compounds to the DGT moulding were very low. PES filter membrane and agarose diffusive gel were selected for the development of the DGT devices. Although the adsorption of PFASs on both agarose crosslinked polyacrylamide (APA) and agarose gel is similar (Figure S1), agarose gel was chosen as it has larger pore size (estimated >100 nm) compared to APA polyacrylamide gel (estimated pore size of <20nm) [45].For the uptake of PFASs on the binding gels, the WAX and MAX based gels showed nearly 100% adsorption for all 12 compounds, while XAD18 and HLB based gels showed less than 70% adsorption for short-chain PFASs (Table S2). The order of ability to bind the studied PFASs is listed: WAX = MAX > HLB > XAD18 (Table S2). Since the *p*Ka of PFCAs is estimated as < 3.5 and that of PFSAs is much lower than similar carboxylic acids, they are mainly negatively charged at ambient pH values.[11] WAX and MAX resins are anion exchangers and can effectively bind the 12 PFASs. HLB resin has hydrophilic N-vinylpyrrolidone groups, and can interact with both apolar and polar organic molecules. Although it can bind negatively charged chemicals with polarity, the adsorption efficiency and rate should be lower than the anion exchanger based resins which are designed specifically for anionic compounds[46]. The study of Gobelius, L. et al.[47] supports this inference. XAD18 is a macroporous adsorbent resin without anion exchange groups, and it is not specially designed for the adsorption of ionic compounds . Therefore, the adsorption of PFASs on XAD18 resin is not substantial. . Hence WAX and MAX gels were used as the binding layer of DGT samplers and for the elution efficiency tests.

Elution Efficiencies. The WAX and MAX binding gels were loaded with known amounts of PFASs and then eluted. The elution efficiencies for WAX binding gels were in the range of 93.1-109% (Table S3). As for MAX binding gels, five PFCAs and two novel PFASs - most of which have a carboxylic acid group - were in the range 79.7-96.5% and the other five PFSAs (which have a sulfonic acid group) were much lower (37.7% -53.3%) (Table S4). This was similar to those for anionic pesticides using MAX binding gels.[40] This may be because compounds with carboxylic acid groups were more lipophilic than those with sulfonic acid groups, and could be more easily eluted by methanol (6:2 FTSA has a sulfonic acid group too, but its long carbon chain enhanced its lipophilicity). Based on the elution efficiency, WAX-DGT was chosen for further testing and development work.

Uptake kinetics. Mass of the 12 PFASs by accumulated on the WAX binding gels increased linearly in the first 40 minutes of the uptake experiment and reached 80% of maximum binding within 100 minutes (Figure S2). The average uptake rate of PFOA during the first 10 mins was 4.42 ng cm^{-2} min^{-1}, while that for PFOS was 5.32 ng cm^{-2} min^{-1}. WAX binding gels had faster uptake rates of PFOA and PFOS than XAD18 binding gels (the average uptake rates of PFOA and PFOS by XAD18 binding gels in the first 10 mins were 2.86 and 3.65 ng cm^{-2} min^{-1}, respectively[35]). The average rates for other studied PFASs by WAX binding gels were in the range of 4.03–5.32 ng cm^{-2} min^{-1}, considerably higher than the required flux (0.23-0.44 ng cm^{-2} min^{-1}) by DGT sampler equipped with 0.75 mm agarose diffusive gel[35]. These results show that the WAX gel can bind the 12 PFASs quickly, keeping the concentration at the interface between the binding gel and diffusive gel effectively zero, which is the key criteria for high accuracy of DGT measurements.[25]

Diffusion coefficients of PFASs. It is essential to obtain reliable diffusion coefficients for the diffusive gel, in order to use eq. 1 to calculate C_{DGT} accurately. The diffusion cell experiments show that the masses of PFASs diffusing from the source compartment to the receptor compartment of the device increase linearly with the diffusion time (Figure S3). The diffusion coefficients, D_{cell}, of the 12 PFASs obtained from the slope in Figure S3 using eq. 2 were in the range from 4.55×10^{-6} to 6.46×10^{-6} cm^2 s^{-1}; all the values are listed in Table 1. Diffusion coefficients obtained from the deployments of DGT samplers in solution with known concentrations of PFASs, D_{DGT}, were similar to the values of D_{cell} with ratios of 1.01 ± 0.06 (Table 1), implying good reliability of the diffusion coefficients measurements. Guan et al.[35] measured diffusion coefficients of PFOA and PFOS using a polypropylene-based diffusion cell device, obtaining values of 4.37×10^{-6} and 5.08×10^{-6} cm^{-2} s^{-1} at 25°C respectively, while the diffusion coefficients were 4.89×10^{-6} and 4.55×10^{-6} cm^{-2} s^{-1} at 25°C measured using a stainless-steel diffusion cell device in this study. The slight difference in D values may be due to possible adsorption of PFOA and PFOS on polypropylene material. We therefore suggest stainless-steel is a better material for the diffusion cell device when testing organic chemicals.

The diffusion coefficients (*D*) in the diffusive gel decreased linearly ($r^2 = 0.97$ for PFCAs and 0.96 for PFSAs) with increasing perfluoroalkyl chain lengths (CF_2) for the five chemicals in the PFCAs group and the five chemicals in PFSAs group (Figure 1). As the CF_2 increases, the hydrophobicity of the PFCAs and PFSAs increases and hence the *D* values of target analytes decrease in the agarose diffusive gels. It is noteworthy that functional groups such as the carboxylic acid and sulfonic acid groups also affected the *D* value. For example, although PFPeA and PFBS both have four perfluoroalkyl carbons, the diffusion coefficient of PFBS is higher than PFPeA. The equations obtained from the linear fitting lines can be used to derive *D* values of PFASs with the same functional group. These can be used to estimate *D* values of other PFASs not investigated here, if it is necessary to undertake emergency monitoring, for example. It is interesting to note that 6:2 FTSA has a similar *D* value to PFOS and the carbon chain length of the two compounds is similar too. However, the *D* value of GenX is different from all the PFCAs, likely because of its different carbon chain structure. Therefore, it can be inferred that the fitting equations in Figure 1 can also be used on the compounds that have similar carbon chain structures to PFCAs and PFSAs.

Perfluoroalkyl compounds are more than 10,000 compounds in total, as estimated by the US Environmental Protection Agency. As there are so many PFASs, it is therefore practical to use fitting equations to calculate diffusion coefficients of each compound in the same subtype, to efficiently expand the application of DGT for screening/monitoring PFASs. This strategy may promote application of the DGT technique for the screening, monitoring and investigation of more organic pollutants in the environment. However, not all perfluoroalkyl compounds share the same ion type. Therefore, more work is needed for *D* value prediction, and direct measurement of *D* values is needed to give the most reliable measurements of new compounds by DGT.

DGT Performance under Different Conditions. *pH.* pH in natural waters varies widely and its change may potentially affect the uptake of target analytes by binding gels. Most PFASs measured by WAX-DGT samplers in solutions with pH ranging from 3.03-8.96 had similar ratios of C_{DGT} to C_{soln} about 1.0 ± 0.1 (Figure 2). There were exceptions at pH 8.13 and 8.96, where the ratios were ~0.64 and 0.41 for PFBA, indicating the DGT measured concentrations were significantly lower than the concentrations in the solution. The ratios were also slightly below 0.9 for PFPeA and PFBS.

The *p*Ka of WAX resin is ~6, and the charged state of WAX resins will change with pH. When the pH is greater than 8, WAX resin is completely deprotonated and is uncharged. In such conditions, some PFASs (such as PFBA) may not be effectively bound by ion exchange. However, some other interactions (such as hydrophobic interactions) may be involved in the binding[48], hence improving the performance of WAX binding gels at high pH.

Ionic strength. When WAX-DGT samplers were deployed in solutions of different ionic strength (ranging from 1 to 500 mmol L^{-1}), the DGT measured concentrations of all 12 PFASs were very close to their concentrations in solution, with the $C_{\mathrm{DGT}}/C_{\mathrm{soln}}$ ratio ~1.0 ± 0.1 (Figure S4). This indicates that the ionic strength in this range will not affect the performance of WAX-DGT samplers and means that the WAX-DGT sampler can be used to measure PFASs across the range of freshwaters to seawater.

DOM. Dissolved organic matter (DOM) is ubiquitous in natural waters, with an average concentration of 5.7 mg L^{-1}.[49] The DOM contents in polluted water and wastewater from sewage treatment plants are normally higher. Humic acid was used to test the effect of DOM (across the range 0-30 mg L^{-1}) on performance of WAX-DGT samplers. There was no obvious effect on DGT measurements of PFASs, as the ratios of $C_{\mathrm{DGT}}/C_{\mathrm{soln}}$ were all within 1.0 ± 0.1 (Figure S5).

Binding Capacity. Whether DGT technology can be used to measure PFASs in aquatic systems over long-term deployments or/and monitor those chemicals in polluted environments depends on the binding capacity of the resin gel used in DGT samplers. The masses of target analytes accumulated by WAX-DGT samplers increased linearly with increasing concentrations in deployment solutions (Figure S6), following the theoretical prediction by eq. 1 (except for PFBA). The binding capacity of PFBA was about 30 μg per DGT sampler, while other analytes were all at least 40 μg per DGT sampler. The results show that each sampler can bind more than 440 μg of PFASs in total. According to previous studies, the concentrations of PFASs were <1 μg L^{-1}, even in raw wastewater[13]. WAX-DGT can be deployed for >2 months in this condition without exceeding capacity, as calculated using eq. 1. As the maximum binding capacity was not reached in the experiment (no levelling-off in Figure S6, except for PFBA), the true capacity could be much higher than 440 μg per sampler. It is easily sufficient for application in a wide range of field deployments, even considering the competition effects between the PFASs. Therefore, although the maximum binding capacity was not reached (no levelling-off in Figure S6, except for PFBA), the capacities obtained are easily sufficient for application in a wide range of field deployments. Even for PFBA, the binding capacity is high enough for field deployments in polluted environments.

Deployment time. It is necessary to study the response of DGT measurements to the deployment time, because the concentrations of PFASs are usually in the ng mL^{-1} level in the environment and DGT samplers need to be deployed in waters for long enough time to accumulate detectable levels. Masses of the 12 PFASs measured by WAX-DGT increased linearly with the deployment time (3-168 h) (Figure S7), and also in good agreement with the theoretical values predicted using DGT equation 1.

Field application of WAX-DGT samplers. The instrument quantitation limits (IQLs), DGT blanks and method quantitation limits (MQLs) of DGT samplers were assessed prior to further testing of the samplers in field conditions. The results are given in Table S7, along with the discussions. The results show that WAX-DGT samplers with UPLC-MS/MS give the sensitivity, precision and reliability to measure PFASs in natural waters.

Application in WWTP. The concentrations of the PFASs in the influent and effluent of an urban/industrial WWTP in Suzhou were determined for grab samples and WAX-DGT samplers. The results are presented in Figures 3, S10 and S11. The distribution patterns of PFASs were similar in grab and DGT samples (Figure 3). However, the concentrations of PFASs obtained by the two sampling approaches are different and the concentrations in grab samples in both influent and effluent fluctuated widely during the 12 days sampling period (Figures S10 and S11). It is believed this variation is attributed to irregular discharges of industrial wastewater. Grab sampling is susceptible to such variation, whilst the DGT-measured concentrations integrate PFASs concentrations over time (Figures S10 and S11). PFHpS was not detected by either grab sampling or DGT samplers in the influent or effluent. GenX was detected in the influent but was not detected in the effluent, suggesting that the WWTP removed GenX effectively from the influent. PFPeS and 6:2 FTSA were detected by DGT samplers in both influent and effluent and in the grab samples of influent, but not in effluent grab samples. There could be two possible reasons: i) the occurrence of PFPeS and 6:2 FTSA is different from PFHxS in the effluent due to the water treatment processes and stabilities of the compounds. We think these compounds can be removed efficiently by the treatment process, when it is operating well. However, the treatment processes may not be stable, so that it may be sub-optimal for some days during our 12 days experiment. We collected water samples every 3 days, so grab sampling may have missed such an event. However, such variability would be integrated and captured by DGT, which samples continuously over the deployment period; ii) the disappearance of PFPeS and 6:2 FTSA in grab samples during transport and storage due to possible adsorption or/and degradation processes. This has demonstrated clearly the advantage of DGT passive sampling over grab sampling for those chemicals.. As shown in Figures S10 and S11, the mean concentrations for the grab samples are in agreement with the DGT measured concentrations, with of the ratio of 0.9-1.1 for most of the PFASs. This supports the view that DGT averages the high variability of the grab samples to give

TWA concentrations.

Application in Rivers. As noted earlier the Qinhuai River is the largest urban river in Nanjing and a tributary of the Yangtze River. The Yunliang River is one of the tributaries to the Qinghuai River. They are all likely to be heavily impacted by urban, industrial and WWTP discharges; our expectation when the sites were selected was that concentrations in the Yangtze River site may have somewhat lower concentrations than the QH and YN sites, because of its much greater volume/dilution effect.

Figure 4 presents a comparison of the DGT measured concentration (12-day deployment) and the concentrations obtained by grab sampling at five time points during the same period (see also Figures S12, S13 and S14). The distribution and the proportion of PFASs were similar between grab sampling and DGT measurement (Figure 4). Similar to the grab sampling at the WWTP, the concentrations of the PFASs in the YN and QH Rivers fluctuated during the sampling campaign, possibly caused by the irregular discharges of WWTP and urban point sources. There was close agreement between the concentrations obtained by DGT and averaged grab samples (see Figure 4 and Figures S12, S13 and S14). The profiles were dominated by PFOA and PFOS – generally the most abundant and priority PFASs in all three rivers; PFBA and PFBS were also quite abundant, especially in the YN samples (see Figure S12). As expected, concentrations in the YZ samples were lower overall (Figure 4) due to greater dilution effect, but were still relatively high and impacted by the collective discharges from major conurbations upstream of Nanjing (e.g. Hefei, Wuhan, Chongqing). PFHpA had similar low concentrations in three rivers and the concentration of PFHxA in the YZ

River was much higher than other two rivers. As expected, the number of compounds detected in the three rivers was lower than in the WWTP study. Specifically, PFPeS, PFHpS, 6:2 FTSA and GenX were not detected in the three rivers; PFHxS was not detected in the YN River and the YZ River and PFPeA was not detected in the YZ River. All these compounds were detected in the WWTP.

Environmental Implications. We have developed and validated the WAX-DGT passive sampler for a range of traditional and emerging PFASs, including those which are the most widely used currently. Laboratory characterization and field applications have demonstrated the stability and reliability of these samplers. They can be conveniently deployed and accurately measure concentrations of target PFASs in rivers and wastewaters. However, more work is needed to test the stability and reliability of DGT in different environmental conditions. The linear relationships between diffusion coefficients of PFASs in the diffusive gel and perfluoroalkyl chain lengths (CF_2) of PFASs with different functional groups can help to extend the application of DGT for screening, monitoring and studies of other PFASs. There are currently many hundreds of other anionic PFASs which have been synthesized and future work will need to screen for their presence in the environment, to help prioritise those which require regular monitoring and risk assessment. Because of the large number of perfluoroalkyl compounds, it is not realistic to directly determine the diffusion coefficient of each compound for full quantitative analysis. However, this study provides a method to calculate diffusion coefficients of other PFASs from a knowledge of those quantified here, which will expand the application scope of DGT for semi-quantitative screening of the wide array of PFASs. Under the Stockholm Convention, PFOS, PFOA and other PFASs must be monitored in aquatic systems, to help identify national and regional scale sources and assess temporal trends. The DGT technique is ideally suited for such work, since it provides reliable time-weighted average concentrations, ideal for catchment scale monitoring and source identification purposes.

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Associated Content in the Supplementary Material

Detailed information on theory of DGT, detailed information of reagents, materials, and solutions, detailed information on methods to water sample extraction, check potential adsorption onto materials, comparison and selection of adsorption resins, aging effect, chemical analysis and QA/QC; results and discussion on potential adsorption onto materials, DGT blanks and method quantitation limits, competition among different PFASs and aging effect, the responses of DGT samplers to the diffusion layer thickness; and tables and figures of tested chemicals, adsorption efficiency, elution efficiencies, optimized mass spectrum parameters, UPLC gradient program, IQL, DGT blanks and MQL for DGT technique and solid phase extraction (SPE) spike recovery, competition effect, basic parameters of sampling point, potential adsorption onto materials, uptake kinetics, diffusion coefficients, effects of IS, DOM, capacity, deployment time, diffusive gel thickness, and storage time of binding gel on DGT performance and concentration of PFASs in WWTP and freshwater.

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Table 1. Diffusion coefficients (10^{-6} cm^2 s^{-1}) of the 12 PFASs obtained at 25 °C using a diffusion cell device (D_{cell}) and by deploying WAX-DGT ($^{\mathrm{WAX}}D_{\mathrm{DGT}}$) in solution with known concentrations of PFASs for 24 h.

PFASs	D_{cell}	$^{\mathrm{WAX}}D_{\mathrm{DGT}}$	$D_{\mathrm{cell}}/^{\mathrm{WAX}}D_{\mathrm{DGT}}$
PFBA	6.46	6.61	0.98
PFPeA	6.06	5.95	1.01
PFHxA	5.87	5.78	1.02
PFHpA	5.33	5.36	0.99
PFOA	4.89	5.14	0.95
PFBS	6.22	6.24	1.00
PFPeS	5.87	5.72	1.03
PFHxS	5.62	5.43	1.03
PFHpS	5.04	5.06	1.00
PFOS	4.55	5.07	0.90
6:2 FTSA	4.96	5.27	0.94
GenX	5.00	4.77	1.05

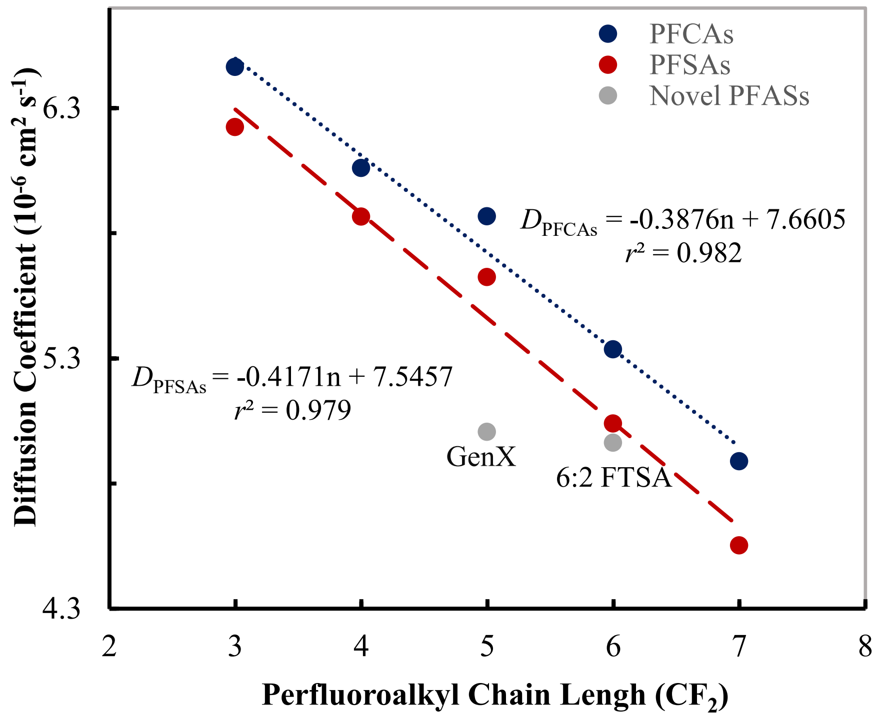

Figure 1. Relationship between diffusion coefficients (*D*) and perfluoroalkyl chain lengths (CF_2) of the studied PFASs presented according to their functional group. Dark blue round symbols represent PFCAs. Red round symbols indicate PFSAs. Grey round symbols mean GenX and 6:2 FTSA from left to right, respectively. The dark black dotted line is the linear fitting line between *D* values and perfluoroalkyl chain lengths of PFCAs. The red dash line is the linear fitting line between *D* and perfluoroalkyl chain lengths of PFSAs.

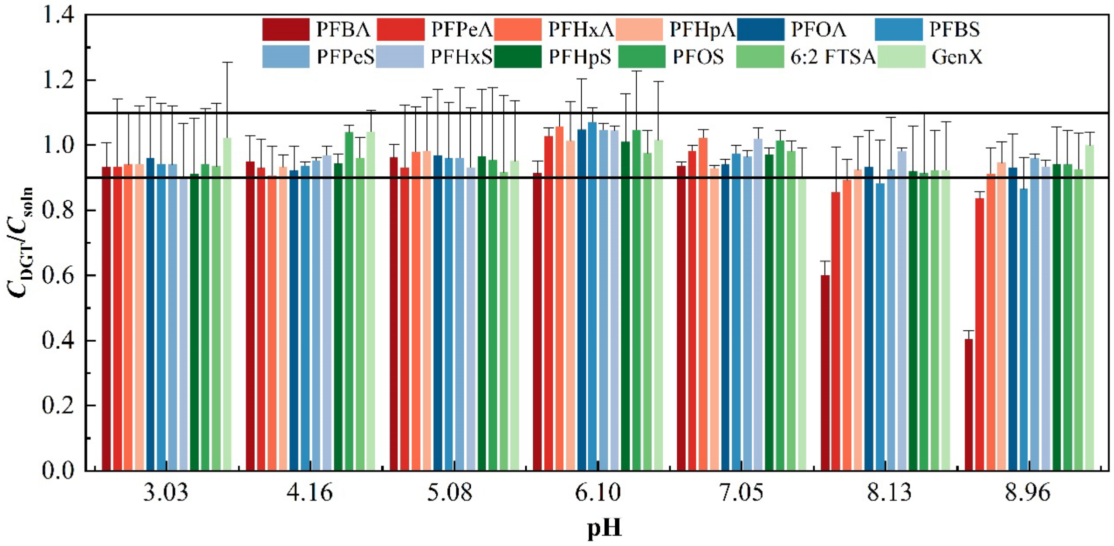

Figure 2. Effect of pH on the ratios of concentrations measured by WAX-DGT, C_{DGT}, to deployment solution concentrations, C_{soln}, for the 12 studied PFASs. DGT samplers equipped with 0.14 mm thick PES filter membrane, 0.75 mm thick agarose diffusive gel and 0.5 mm thick WAX binding gel were immersed in continuously stirred 2 L of 20 µg L^{-1} PFASs solution with pH ranging from 3.03 to 8.96 at 25°C for 24 h. Exposure window area of the DGT device is 3.14 cm^{2}. IS = 0.01 mol L^{-1} NaCl and DOM = 0 mg L^{-1}. Solid lines represent the target values of 0.9 and 1.1. Error bars indicate the standard deviation of three replicates.

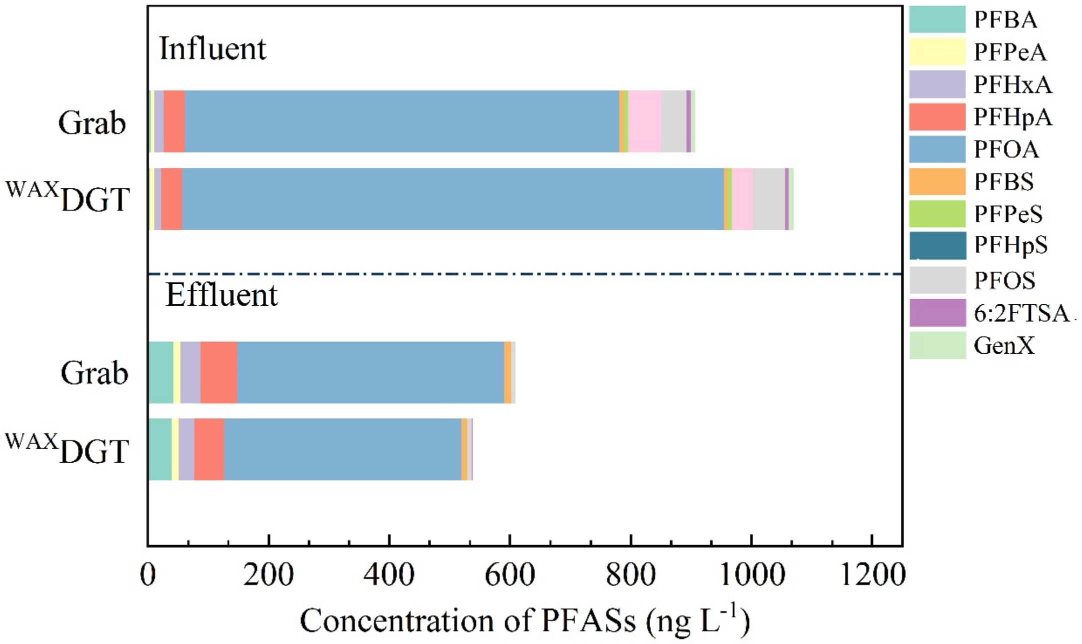

Figure 3. Concentrations of PFASs in the influent and effluent of a WWTP measured by grab sampling and WAX-DGT samplers.

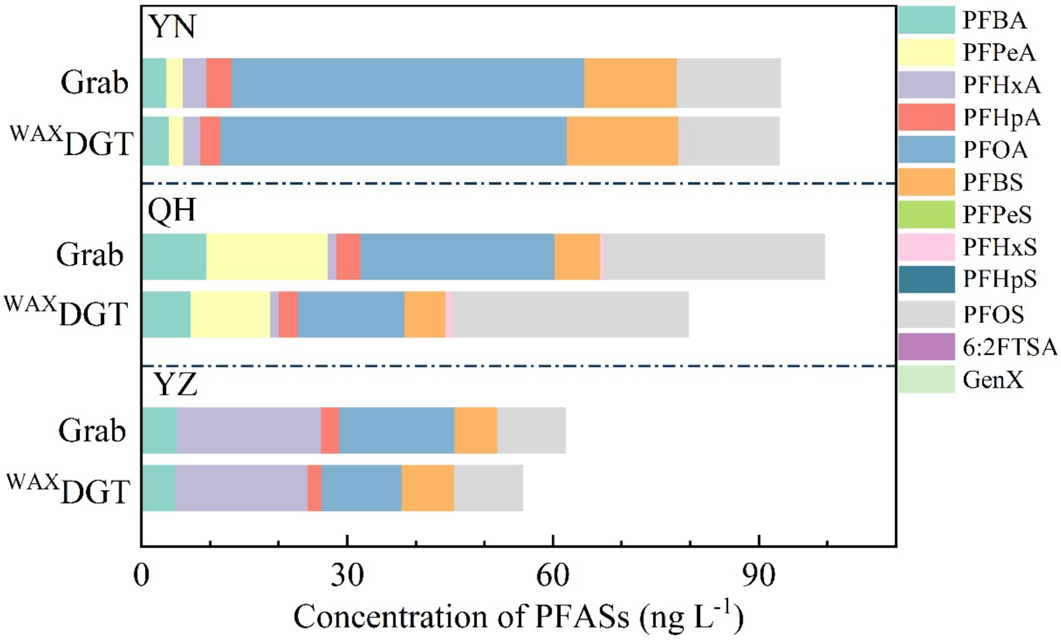

Figure 4. Concentrations of PFASs at the YN, QH and YZ sampling points in three freshwater rivers measured by grab sampling and WAX-DGT samplers.

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