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Activated Charcoal Based Diffusive Gradients in Thin Films for in Situ Monitoring of Bisphenols in Waters

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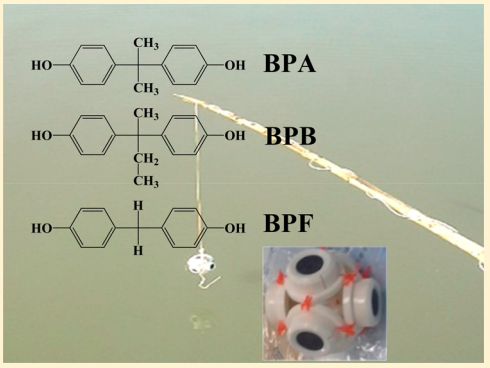
Supporting Information

ABSTRACT: Widespread use of bisphenols (BPs) in our daily life results in their elevated concentrations in waters and the need to study their environmental impact, which demands reliable and robust measurement techniques. Diffusive gradients in thin films (DGT) is an in situ passive sampling approach which provides time-integrated data. In this study we developed a new methodology, based on DGT with activated charcoal (AC) as a binding agent, for measuring three BPs (BPA, BPB, and BPF) which incorporated and tested its performance characteristics. Consistent elution efficiencies were obtained using methanol when concentrations of BPs were low and a methanol−NaOH mixture at high concentrations. The diffusion coefficients of BPA, BPB, and BPF in the diffusive gel, measured using an independent diffusion cell, were 5.03×10^{-6}, 5.64×10^{-6}, and 4.44×10^{-6} cm^2 s^{-1} at 25 °C, respectively. DGT with an AC binding gel had a high capacity for BPA, BPB, and BPF at 192, 140, and 194 μg/binding gel disk, respectively, and the binding performance did not deteriorate with time, up to 254 d after production. Time-integrated concentrations of BPs measured in natural waters using DGT devices with AC gels deployed in situ for 7 d were comparable to concentrations measured by an active sampling method. This study demonstrates that AC-based DGT is an effective tool for in situ monitoring of BPs in waters.



Endocrine-disrupting chemicals, including bisphenols (BPs), are widely used as base chemicals in the manufacture of polycarbonate plastics and the resin lining of food and beverage cans[1−4] and thus are commonly found in daily life. As such, they inevitably enter the environment and are found in rivers, bottled water, and even tap water.[5−7] Reported concentrations of BPs, which range from 0.5 to 16 ng/L in rivers for bisphenol A (BPA)[5] and from 0.85 to 1.5 μg/L in wastewaters for bisphenol F (BPF),[7] can adversely affect ecosystems and human health. Human exposure to BPA may elevate the risk of obesity, diabetes and coronary heart diseases,[8] while bisphenol B (BPB) and BPF induce moderate to slight acute toxicity and have an estrogenic activity similar to that of BPA.[9] The global demand for BPs is still growing. For example, demand for BPA grew from 3.9 million tons in 2006 to about 5 million tons in 2010.[10] Therefore, determination of the concentrations of BPs in aquatic ecosystems is necessary to further understand their possible effect on aquatic organisms and human beings.

Active sampling approaches, which collect water samples on site and return them to the laboratory for analysis, have been used extensively for monitoring organic contaminants. They provide a snapshot of pollutant concentration at a certain time of sampling and are usually time-consuming and costly. Passive sampling devices, which accumulate analytes during their in situ deployment, provide an alternative approach which overcomes these limitations. One type of sampler, named the polar organic chemical integrative sampler (POCIS), has successfully been used for monitoring polar organics, including BPs.[11] However, a drawback of POCIS is that the conditions of the laboratory calibrations used to estimate the sampling rate are likely to differ from field conditions. For example, water temperature, flow rate, and turbulence could affect the sampling rates and estimates of analyte concentrations in water.[12] The thickness of the ubiquitous layer of solution at the surface of the device, known as the diffusive boundary layer (DBL), changes along with the field conditions, but this is not accommodated in calculating the concentrations of BPs. Consequently, inaccurate estimations of the concentrations of BPs may be obtained if POCIS is used.[13]

Another passive sampling technique, diffusive gradients in thin films (DGT),[14] has the potential to provide concentrations with improved performance compared to other passive samplers. DGT is well established for measuring labile

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inorganic species in aquatic environments.[15,16] Recently, Chen et al.[17−19] successfully used this sampler with XAD18 as the binding agent to measure antibiotics in waters and soils. These studies paved the way for extending the use of DGT to monitor further trace organics in waters. The DGT measurement, C_{DGT}, provides the time-integrated concentrations of organics in the solution by the use of the following equation, which is derived from Fick's first law of diffusion:[15]

$$C_{DGT} = \frac{M(\Delta g + \delta)}{DAt} \quad (1)$$

The measured mass of a target organic accumulated on the binding gel is M, the thickness of the material diffusion layer within the device is Δg, the DBL thickness is δ, the diffusion coefficient of the organics in the diffusive gel is D, the deployment time of DGT devices is t, and the DGT sampling area exposed to the bulk solution is A. Typically, the thickness of the diffusion layer in solution, δ, is much smaller than that in the device, Δg (~0.9 mm), making the DGT measurement fairly insensitive to the hydrodynamic conditions.[20] Under well-stirred conditions, δ can be neglected.[21]

Recently, Lucas et al.[22,23] used activated charcoal as the binding layer in DGT to measure labile gold in natural waters. This binding material is known to be effective at removing BPs from wastewater.[24,25] In the present study, we prepared DGT devices with binding layers comprising activated charcoal (AC) incorporated into agarose gel. In evaluating the performance characteristics of the new DGT device for measuring three BPs, i.e., BPA, BPB, and BPF, the binding kinetics, elution efficiency by different eluents, and capacity of the binding gels were studied, along with the possible effects of pH, ionic strength, deployment time, competition among different BPs, diffusive gel thickness, and storage time of the binding gels. The DGT devices containing AC gels were deployed in natural waters, and the measured concentrations were compared with those from conventional active sampling.

EXPERIMENTAL SECTION

Reagents, Materials, and Solutions. All containers and pipets were made of glass. Standard DGT moldings of acetonitrile−butadiene−styrene (ABS) were obtained from DGT Research Ltd., United Kingdom. Holders for the DGT devices used for deployments were made of stainless steel. Stock solutions of BPA (Sigma-Aldrich, >99%), BPB (TGI, >98%), or BPF (TGI, >99%) were prepared at 5000 mg L^{-1} in methanol (HPLC grade) and stored in sealed amber glass bottles at −20 °C. MQ (Milli-Q, Millipore, United States) water was used to dilute stock solutions. Powdered AC (100−200 mesh) was purchased from Sigma-Aldrich. Four different filter membranes, i.e., hydrophilic poly(tetrafluoroethylene) (PTFE), mixed cellulose ester (MCE), nylon (NL), and poly(ether sulfone) (PES), with diameters of 25 mm and pore sizes of 0.45 μm, were purchased from Shanghai Anpel Scientific Instrument Co., except PES, which was from Pall Co., United States.

Chemical Analysis. High-performance liquid chromatography (HPLC) coupled with a fluorescence detector was used to analyze BPs for samples from laboratory evaluations (details in the Supporting Information). BPs in the samples from field trials were analyzed by LC−MS/MS following a published procedure[26,27] (details in the Supporting Information).

Assessment of Possible Adsorption. Diffusive gels and the filter membranes were soaked in 10 mL of 100 μg L^{-1} BPA, BPB, or BPF solutions and then shaken horizontally for 6 h. Due to their large size, DGT moldings were soaked in 200 mL solutions. The concentrations of BPs in the solutions before and after exposure were measured to obtain the mass adsorbed.

Diffusive and Binding Gel Preparation. Diffusive gel was prepared according to a previously reported procedure using agarose.[28] In short, 1.5% agarose solution was prepared by dissolving 0.45 g of agarose in 30 mL of MQ water and then heated until the solution became transparent. The hot gel solution was immediately pipetted into preheated, gel-casting molds, comprising two sheets of glass separated by 0.75 mm thick spacers, and left to cool to its gelling temperature (~36 °C). The gels were cut into disks (2.51 cm in diameter) and stored in 0.01 M NaCl solution. The binding gel (0.05 cm thickness) was made by mixing 5 mL of AC suspension (obtained by mixing 0.25 g of AC in 5 mL of MQ water) with 20 mL of 1.5% warm agarose solution (>80 °C). The resulting mixture was pipetted into prewarmed molds (glass sheets separated by 0.5 mm thick spacers) and left to cool for 1 h. The gels were cut into disks and stored in MQ water prior to use.

Kinetics and Elution Efficiency. Each AC gel disk was immersed in 10 mL of 100 μg L^{-1} BPA, BPB, or BPF with a matrix of 0.01 M NaCl and shaken for various times from 0.5 min to 24 h. The elution efficiencies of the BPs were obtained by eluting the AC gels loaded with BPs in 10 mL of methanol or a mixed eluent of methanol and NaOH (7 mL of methanol + 3 mL of 1 M NaOH, 7 mL of methanol + 3 mL of 0.5 M NaOH, or 9 mL of methanol + 1 mL of 1 M NaOH) (n = 6) for at least 24 h to investigate the appropriate elution conditions. The pH of the eluents using the mixed eluent was adjusted to within the range of 4−8 using 1 M HCl and 1 M NaOH before analysis. The eluents and immersion solution were analyzed to calculate the elution efficiency.

Diffusion Coefficient Measurement. Diffusive coefficients of BPs were measured using a previously described diffusion cell[28] with minor modification. In brief, the cell consisted of two glass compartments connected by a circular window (1.5 cm in diameter) containing a 0.80 mm thick agarose-based diffusive gel. Both compartments were rinsed with methanol and subsequently MQ water. The solution in the source compartment contained 50 mL of 2 mg L^{-1} BPA, BPB, or BPF. The pH and ionic strength (IS) were the same as those of the solution in the receptor compartment, without BPs. The solutions in both compartments were well stirred during the experiment. An aliquot of 0.2 mL of solution was removed from each compartment at intervals of 15 min. To check the possible effect of pH and IS on diffusive coefficient measurements, experiments were performed under three different conditions: (1) pH 7, IS 0.01 M; (2) pH 4, IS 0.01 M; (3) pH 7, IS 0.1 M. The slope of the linear plot of the measured masses of each BP diffused into the receptor compartment versus time was used to calculate the diffusion coefficient, D:

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

A is the area of the connecting window of the diffusion cell, C is the concentration of BPs in the source compartment, and Δg is the thickness of the diffusive gel.

Diffusion coefficients were also measured by immersing DGT devices equipped with an AC gel, a diffusive gel, and a PTFE filter membrane (see the reason for choosing this

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membrane for the DGT's membrane in the Results and Discussion and Figure 1) in 2.5 L of 100 μg L^{-1} BPA, BPB, or BPF solutions for 12 h. The following equation, transformed from eq 1, was used to calculate the value of D:

$$D = \frac{M(\Delta g + \delta)}{C_{DGT}At} \quad (3)$$

Effects of Ionic Strength, pH, Deployment Time, and Diffusive Gel Thickness. To test the effects of IS and pH on DGT performance, DGT devices with an AC gel, an 0.80 mm thick diffusion gel, and a PTFE filter membrane were deployed for 12 h in various well-stirred solutions: (a) 2.5 L of 10 μg L^{-1} BPA and BPB and 20 μg L^{-1} BPF solution (pH 6) with a range of NaCl concentrations from 0.001 to 0.5 M; (b) 2.5 L solution containing 0.01 M NaCl and 10 μg L^{-1} BPA and BPB and 20 μg L^{-1} BPF at different pH values (5−8, adjusted with 1 M HCl or 1 M NaOH). To evaluate the effect of deployment times, DGT devices were immersed in 2.5 L of well-stirred solutions (pH 6) containing 40 μg L^{-1} BPA, BPB, and BPF and 0.01 M NaCl and then retrieved at different times (from 12 to 168 h). To investigate the relationship between mass accumulated by DGT and diffusive gel thickness, devices containing diffusive gel with different thicknesses (0.050−0.175 cm) were deployed for 12 h in 2.5 L of solution (pH 6) containing 100 μg L^{-1} BPA, 40 μg L^{-1} BPB or BPF, and 0.01 M NaCl.

Capacity, Competition Effects among BPs, and Aging Effects. To measure the capacity for accumulating BPs of AC gels incorporated in DGT, the assembled DGT devices were immersed for 12 h in well-stirred solutions containing 0.01 M NaCl and a range of concentrations of BPs: BPA (0.1−60 mg L^{-1}), BPB (0.1−25 mg L^{-1}), or BPF (0.1−25 mg L^{-1}).

The competition effect among these three BPs in solution was evaluated using different solution concentrations. DGT devices were deployed for 12 h in various well-stirred solutions (2.5 L) containing 0.01 M NaCl: (a) BPA or BPB set at 10 μg L^{-1}, other two set at 100 or 1000 μg L^{-1}; (b) BPF at 20 μg L^{-1}, BPA and BPB at 100 or 1000 μg L^{-1}.

AC gels were stored in MQ water at 4 °C for different times (40, 87, 128, 158, 184, and 254 d) after production. DGT devices containing the long-term-stored binding gel, fresh diffusive gel, and PTFE filter membranes were deployed for 12 h in 2.5 L of well-stirred solution containing ~400 μg L^{-1} BPA, BPB, and BPF and 0.01 M NaCl.

Field Trial. To compare measurements made using DGT and an active sampling method, six DGT devices were assembled into a hexahedral unit, leaving the exposure windows outward. The hexahedral multidevice, together with a temperature button datalogger (Maxim Integrated Products, United States) set to record temperature every half hour, was placed in a nearby river (Jiuxiang River located in Nanjing, China) for 7 days. Water samples were collected on two occasions each day, at around 10:00 a.m and 16:00 p.m.

The water samples were transferred to the laboratory within 10 min, and then BPs were concentrated by a solid-phase extraction (SPE) method (details in the Supporting Information). The retrieved AC gels in DGT samplers were soaked in 10 mL of methanol for 24 h and then evaporated to near dryness followed by redissolving in 2 mL of 100% methanol. The final eluents from SPE and DGT measurements were filtered through a 0.22 μm membrane and transferred to 2 mL amber HPLC sample vials for instrumental analysis.

Statistical Analysis. All DGT laboratory deployments were conducted in at least triplicate and the results expressed as the mean ± standard deviation. Statistical analysis was carried out using SAS software. Statistically significant differences were established using analysis of variance (ANOVA) and least significant difference (LSD) at the 5% significance level.

RESULTS AND DISCUSSION

Adsorption of BPs by DGT Moldings, Diffusive Gels, and Filter Membranes. Suitable materials and filter membranes used in DGT are necessary to avoid adsorption of BPs, which compromises their measurement. Thus, four types of membrane filters (PES, MCE, NL, and PTFE), together with ABS DGT moldings (including pistons and caps) and diffusive gels, were assessed for their possible adsorption of BPs. Figure 1 shows there was little adsorption of BPs onto the DGT moldings and agarose diffusive gel (<3%). BPs were adsorbed substantially by three types of filter membranes: PES (>95%), MCE (>30%), and NL (>40%). They were not adsorbed appreciably on PTFE membranes (<3%) (Figure 1). Hence, the ABS DGT moldings, agarose gel, and PTFE filter membranes were used throughout this work.

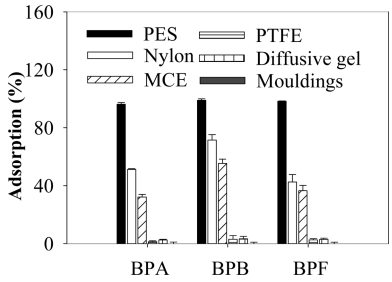

Figure 1. Adsorption of BPA, BPB, and BPF onto DGT moldings, diffusive gels, and four different filter membranes. Error bars were calculated from the standard deviation of three replicates.

Sorption Kinetics of BPs onto Activated Charcoal Gel. The uptake of BPs by AC gel increased linearly with time for the first 30 min (Figure 2; Figure S1, Supporting Information) and then increased more slowly up to 60 min. After 60 min, almost 95% of the BPs in solution were adsorbed. The average binding rates over the first 30 min for BPA, BPB, and BPF were 2.19, 1.94, and 2.52 ng cm^{-2} min^{-1}, respectively. These rates were much higher than those (0.39, 0.25, and 0.41 ng cm^{-2}

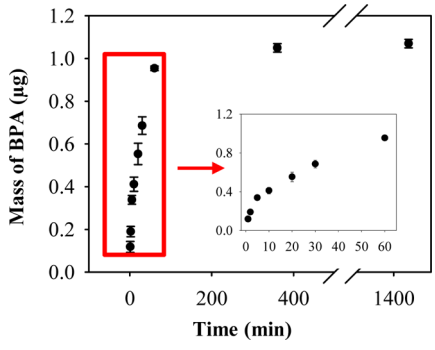

Figure 2. Time dependence of the mass of BPA accumulated by activated charcoal gel in 10 mL solutions containing 100 μg L^{-1} BPA and 0.01 M NaCl. Error bars are calculated from the standard deviation of the replicates (n = 3).

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min^{-1} for BPA, BPB, and BPF, respectively) calculated for DGT devices deployed in a solution containing a 100 $\mu g\ L^{-1}$ concentration of the three BPs at 25 °C. The difference suggests that BPs bind onto the AC gels within DGT sufficiently rapidly to ensure that the concentration of BPs at the diffusive gel/binding gel interface is effectively zero, validating the use of eq 1.

Elution Efficiencies of BPs. Reliable elution efficiencies of BPs from loaded AC gels are needed in calculating C_{DGT}. In this study, we tried four different eluents. The average elution efficiencies of BPA and BPB using 10 mL of methanol were 56.4 ± 2.0% and 95.7 ± 3.3%, respectively (Table 1). However,

Table 1. Elution Efficiencies (%) of BPA, BPB, and BPF from Activated Charcoal Binding Gels Eluted by Different Eluents (n = 6)

eluent[a]	BPA	BPB	BPF
A	56.4 ± 2.0	95.7 ± 3.3	34.5 ± 2.1[b]
			80.4 ± 3.7[c]
B	51.6 ± 2.4	62.1 ± 2.4	54.8 ± 3.0
C	46.4 ± 2.8	60.8 ± 3.8	49.6 ± 2.3
D	43.6 ± 4.3	64.6 ± 2.4	55.2 ± 6.3

[a]Key: A, 10 mL of methanol; B, 7 mL of methanol + 3 mL of 1 M NaOH; C, 7 mL of methanol + 3 mL of 0.5 M NaOH; D, 9 mL of methanol + 1 mL of 1 M NaOH. [b]Stable elution efficiencies when the bound mass of BPF is <1 μg. [c]Stable elution efficiencies when the bound mass of BPF is >100 μg.

for BPF, the elution efficiency varied with the adsorbed mass of BPF on the AC gels (Figure S2, Supporting Information). When the adsorbed mass was less than 1 μg/AC gel disk, the elution efficiency was stable at 35%, but if the adsorbed mass was larger than 1 μg/disk, the elution efficiency increased with the adsorbed mass. When the adsorbed mass reached 100 μg/disk, the elution efficiency was 80% (Figure S2). To overcome this problem of variable elution efficiency, a mixed eluent of 7 mL of methanol and 3 mL of 1 M NaOH was chosen. The obtained elution efficiency of BPF using the mixed eluent was stable at 55% when the adsorbed mass varied from 0.1 to 30 μg/gel disk (Figure S3, Supporting Information). A similar performance was reported by Zhang et al.[29] when eluting BPF from carbon nanotubes. For BPA and BPB, we obtained elution efficiencies with this mixed eluent of 51% and 62%, respectively. For the other two mixed eluents used, namely, 7 mL of methanol + 3 mL of 0.5 M NaOH and 9 mL of methanol + 1 mL of 1 M NaOH, the obtained elution efficiencies of the BPs were close to that for 7 mL of methanol + 3 mL of 1 M NaOH (Table 1). The use of NaOH had little effect on the elution efficiency of BPA, but significantly decreased the elution efficiency of BPB from 96% to 61−65%, so a composition of 7 mL of methanol + 3 mL of 1 M NaOH was chosen as the best compromise eluent for binding layers of DGTs used in laboratory deployments, where there were high BP concentrations in solution and analysis was by HPLC. However, 10 mL of methanol was still chosen as the eluent for field trial samples where low concentrations in solution led to a low content of BPF in the binding gel disk (<1 μg/gel disk).

Diffusion Coefficients in the Diffusive Gel. To calculate C_{DGT} using eq 1, it is necessary to know the value of D. It was measured independently using a diffusion cell. The standard diffusion coefficient at 25 °C was obtained by correcting the diffusion cell measured D using the following equation:

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

The diffusion coefficient of analyte at the solution temperature t (°C) during the diffusion cell experiment is D_t, and D_{25} is the diffusion coefficient of the analyte at 25 °C (Table 2). For BPA,

Table 2. Diffusion Coefficients of BPA, BPB, and BPF in Diffusive Gels at 25°C Measured Using a Diffusion Cell and DGT Devices[a]

	diffusion coefficient (D) (10^{-6} cm^2 s^{-1})	
chemical	diffusion cell	DGT devices
BPA	5.03 ± 0.28	4.78 ± 0.15
BPB	4.44 ± 0.18	4.66 ± 0.21
BPF	5.64 ± 0.25	5.75 ± 0.17

[a]Error bars were calculated from the standard deviation of three replicates.

at three different pH and/or IS conditions (pH 7, IS 0.01 M; pH 4, IS 0.01 M; pH 7, IS 0.1 M), the diffusion coefficients at 25 °C were 4.71×10^{-6}, 5.16×10^{-6}, and 5.22×10^{-6} cm^2 s^{-1}, respectively. The relative standard deviation (RSD) of these values, of less than 6%, indicated no significant difference between them. Therefore, the average value (5.03×10^{-6} cm^2 s^{-1}) was used as the diffusion coefficient of BPA at 25 °C. For BPB and BPF, the calculated D values at 25 °C were 5.64×10^{-6} and 4.44×10^{-6} cm^2 s^{-1}, respectively.

DGT Blank Concentration and Detection Limits. Table 3 summarizes the DGT blank concentration, instrument limits

Table 3. Gel Blank Concentrations, LODs and LOQs of LC−MS/MS, and MDLs[a]

	gel blank concn	LOD	LOQ	MDL
BPA	nd	0.01	0.10	0.002
BPB	nd	0.11	0.45	0.012
BPF	nd	0.07	0.38	0.008

[a]MDLs were calculated from the LOQ, assuming a deployment time of 168 h at 25 °C with a 0.8 mm thick diffusive gel. Units of micrograms per liter.

of detection (LOD) and quantification (LOQ), and DGT method detection limit (MDL) of BPs. DGT blank concentrations were evaluated by measuring the mass of the BPs, using LC−MS/MS, in AC gels retrieved from DGT devices which were left assembled for 168 h without deployment. No BPs could be detected, indicating no measurable release of BPs from DGT moldings. LOD and LOQ were calculated as the minimum detectable amount of BPs with signal-to-noise ratios of 3 and 10, respectively.[30] MDLs for DGT of 2 (BPA), 12 (BPB), and 8 (BPF) ng L^{-1} were calculated from the LOQ, assuming a deployment time of 168 h at 25 °C with a 0.8 mm thick diffusive gel. For BPA, reported concentrations were 100−320 ng L^{-1} in rivers of southern Spain,[31] 29.6−48.1 ng L^{-1} in the Southern Baltic sea,[32] and 63.6 ± 3.4 ng L^{-1} in the Qinghe River of China.[33] For BPF, reported concentrations were 100−1430 ng L^{-1} in wastewaters of southern Spain[31] and 60−2500 ng L^{-1} in different wastewaters from Granada and Melilla (Spain).[33] BPB was detected in wastewaters from Nanjing, China, at

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concentrations ranging from 6 to 46 ng L^{-1} (unpublished data from this laboratory). Given the much lower values of the MDLs than the reported concentrations, DGT coupled to analysis by LC−MS/MS appears to have adequate sensitivity for water quality monitoring. If the concentrations of BPs were lower than the MDL, a longer deployment time could be used to enhance the cumulative mass and lower the MDLs proportionately.[15]

Effect of pH and Ionic Strength. As the solution pH determines the surface charge density of activated carbon and the charge of BP species,[34] it could affect the performance of DGT. Varying the solution pH from 5 to 8 had no systematic effect on the measurement of BPs by DGT (Figure 3a). This

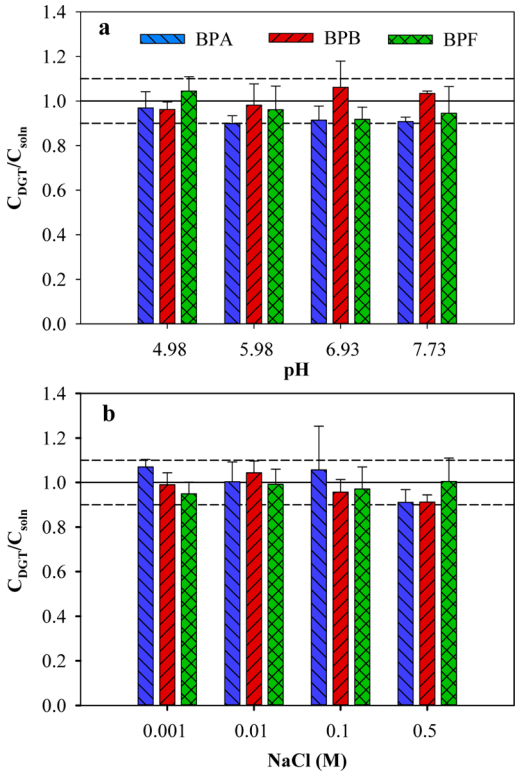

Figure 3. Effect of solution pH (a) and ionic strength (b) on the ratio of DGT-measured BP concentrations, C_{DGT}, to their concentrations in the bulk solutions, C_{soln}. The solid horizontal lines represent the target value of 1, and the dotted horizontal lines represent target values at 0.9 and 1.1. Values are means ± SD of three replicate analyses.

result is consistent with the pK_a of BPA, BPB, and BPF being 10.3[35] and 7.55 and 9.67,[36] respectively. Consequently, BPs in solution with pH in the range from 5 to 8 are mainly in neutral forms, which are more easily adsorbed than ionized species. Moreover, diffusion coefficients of BPs in the diffusive gel were independent of pH (4 and 7). Other workers have reported no effect on BPA removal from wastewater using activated carbon when solution pH was in the range from 2 to 8.[24]

IS could potentially affect the adsorption of BPs on activated charcoal. Higher ionic strength could screen the surface charge of AC, which would favor $\pi-\pi$ interactions and hence enhanced BP adsorption.[37] The presence of NaCl could also cause a salting-out effect, which could decrease the solubility of BPs and also enhance the BP adsorption onto activated carbon.[34,38] As shown in Figure 3b, varying the IS in solution, from 0.001 to 0.5 M NaCl, had no significant effect on the concentrations of BPs. Even at an extremely high IS of 0.5 M, the ratio of DGT-measured concentrations to the independently measured solution concentrations was within acceptable limits (1.0 ± 0.1). The stable diffusion coefficients of BPs in the diffusive gel at different ISs (0.01 and 0.1 M) are consistent with the absence of an IS effect. Measurement of the antibiotic sulfamethoxazole using DGT with an XAD18 binding gel was also unaffected at ionic strengths of 0.001−0.01 M, but affected at an IS of 0.5 M.[17] BPA removal from wastewater using carbon-based materials was little affected by ionic strength up to 0.5 M NaCl.[39] This is consistent with the small effect of IS at 0.5 M NaCl on uptake of BPs by DGT with AC gels.

Capacity. Sufficient capacity of the binding phase for BPs is necessary to ensure their accurate measurement by DGT when they are present at high concentrations or when long-term deployments are used. The mass of BPs bound onto the AC gel used in DGT measurements initially increased linearly with the solution concentration (Figure 4; Figure S4, Supporting

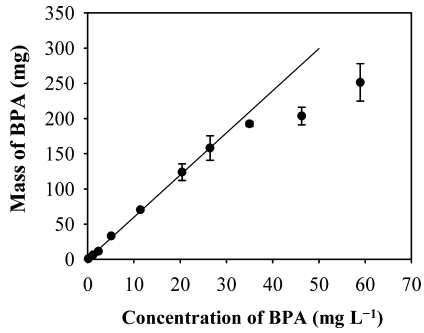

Figure 4. Measured masses of BPA bound onto the activated charcoal gels within DGT devices deployed in well-stirred solutions at different concentrations (0.12−58.9 mg L^{-1}) of BPA. The solid line is predicted from the known solution concentrations using eq 1.

Information) and was close to the theoretical line. The capacities of DGT for BPA, BPB, and BPF were 192, 140, and 190 μg/disk, respectively. Assuming that the concentration in water of each of the BPs was 100 μg L^{-1}, the maximum deployment time before capacity effects compromised the measurements could be more than 3 months. These results show that DGT based on an AC gel is suitable for long-time deployment.

Effect of Deployment Time and Diffusive Gel Thickness. Two experiments investigating the effects of deployment time and diffusive gel thickness on DGT performance were carried out to validate the reliability of eq 1 for calculating concentrations of BPs in waters. The accumulated masses of BPs measured by DGT devices containing AC gels increased linearly with increasing deployment time over 168 h and were fitted well by the theoretical line calculated from the known solution concentration using eq 1 (Figure S5, Supporting Information).

Accumulated masses of BPs measured by DGT devices containing diffusion gels with different thicknesses (0.050−0.175 cm) were proportional to the reciprocal of the diffusive layer thickness (Figure S6, Supporting Information). This indicates that the DBL thickness has little effect on the DGT measurement if the solution is well stirred. These results further support the D values of BPs obtained in this study.

Aging Effect of Activated Charcoal Gel and Competition Effect among BPs. The performance of DGT devices

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containing AC gels, which had been stored in MQ water for 30−254 d from production, are illustrated in Figure S7 (Supporting Information). For all times studied, measurements were, within experimental error, within the expected tolerance of the solution concentration. Therefore, AC gel can be stored in MQ water for up to 8 months and still be used reliably for measuring BPs.

To check whether competitive adsorption between the three BPs affected the DGT measurements, devices were deployed in a series of synthetic solutions having different concentrations (0.01−1.0 mg L^{-1}) of BPs. There was no evidence of any significant effect on the DGT measurements, even at quite high concentrations of the competing BPs (Table S2, Supporting Information).

Field Trial. The good performance characteristics, established in the laboratory, for DGT containing AC gels suggested that it should be an appropriate tool for measuring BPs in natural waters. To establish the reliability of DGT in the real environment, it was deployed in situ in a river for 7 d while water samples were collected twice daily for analysis in the laboratory (an active sampling method). BPA and BPF were detected by both the active sampling method and DGT measurement (Figure 5). Concentrations of BPA and BPF measured by the active sampling approach ranged from 23.8 to 135.2 ng L^{-1} and from 14.7 to 24.8 ng L^{-1}, respectively, with no BPB detected. This range of values of BPA is comparable to those reported for other Chinese rivers, including the Yangtze River estuary (0.98−43.8 ng L^{-1}),[40] Yellow River (12.5−172 ng L^{-1}),[41] and Liao River (12.3−756 ng L^{-1}).[42] The lack of any marked concentration fluctuations observed using the active sampling method demonstrated that during DGT deployment concentrations of BPs were fairly stable. The dotted lines in Figure 5 show the maximum and minimum concentrations measured by DGT, and the solid lines show the average DGT concentrations for BPA and BPF. Almost all data points obtained during the active sampling method were within the maximum and minimum DGT measurements, demonstrating the accuracy of the time-integrated concentrations of BPs measured by DGT.

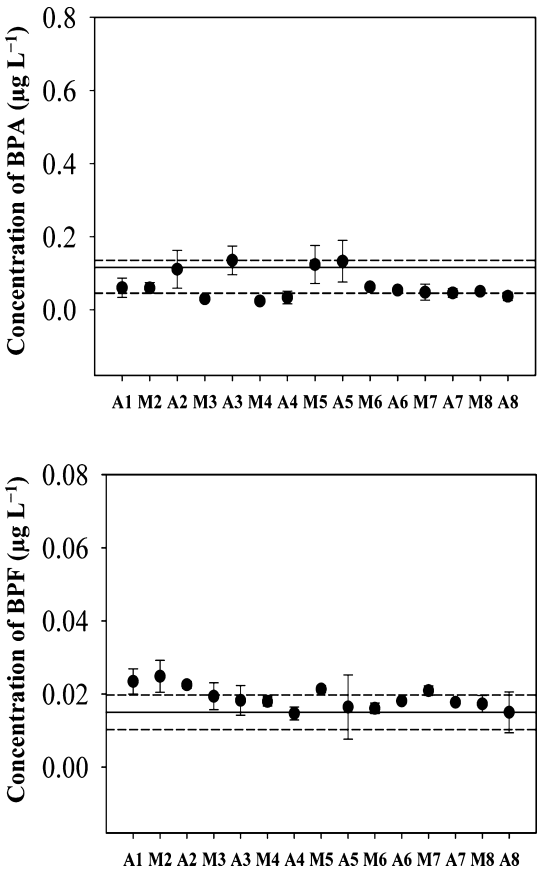

Figure 5. Changes in the concentrations of BPA and BPF during a 7 d sampling campaign. The solid circles represent the concentrations of BPs measured by the active sampling method. The solid line is the time-averaged concentration of BPs measured by DGT, while the upper and lower dotted lines represent the maximum and minimum concentrations of BPs, respectively, measured by DGT. A and M represent afternoon and morning, respectively, in a day. The digit after A or M indicates the day number.

Future Perspective. Although DGT has only been tested for the measurement of these three BPs, it is likely to be capable of measuring other BPs, but further testing is required. Additionally, DGT performance on their breakdown compounds needs to be studied. Development of the DGT technique on overall BPs can be useful for their risk assessment.

Active sampling methods are still widely used for monitoring organic compounds in the environment. However, the limitations of such an approach and the advantages of passive samplers are well recogized.[13] DGT has some advantages over other passive sampling methods, especially its stable sampling rate, which is affected relatively little by the prevailing flow conditions. This work has shown that pH and IS also have little effect on the measurement of BPs by DGT. With DGT, the calculation of concentration can be performed for any in situ temperature because the diffusion coefficient, D, can be corrected for temperature using eq 4. Like other passive samplers, DGT automatically preconcentrates during deployment, and consequently, there is no need for pretreatment of samples in the laboratory. The much smaller size of DGT compared to POCIS makes it less expensive. For example, there is less than 10 mg of activated charcoal on one AC gel disk compared to 200 mg of Oasis HLB in one commercial POCIS device for analyzing BPA.[11]

However, DGT also has its disadvantage compared to other passive sampling methods. The sampling rates for BPA by pharmaceutical POCIS and pesticide POCIS were reported to be 0.117 and 0.0877 L d^{-1}.[11] For DGT, assuming that C_{DGT}/C_{soln} was 1 and the temperature was 25 °C, the sampling rate was 0.013 L d^{-1}. This lower sampling rate for DGT means that a longer deployment time is needed to achieve the same detection limit. In the waters studied here the concentrations were sufficiently high that this lower sensitivity of DGT did not present a problem. Although reducing the thickness of the diffusion gel can increase the sampling rate of DGT, its sensitivity to changes in flow rate would increase, so it is only an option in fast-flowing waters. Detection limits could also be improved by deploying several DGT devices and merging the eluents.[18]

■ ASSOCIATED CONTENT

Supporting Information

Information on analysis methods, including SPE, HPLC, and LC−MS/MS, uptake kinetics of BPB and BPF by AC gels, elution efficiencies of BPs using different eluents, DGT capacity for BPB and BPF, relationship between measured masses of BPs by DGT and deployment time or diffusion layer thickness, SEM images of the AC gel, temperature measured by button

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thermometers, result of competition effects, recovery efficiencies of BPs in spiked MQ water, and physiochemical properties of BPs. 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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