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A diffusive gradients in thin-films technique for the assessment of bisphenols desorption from soils

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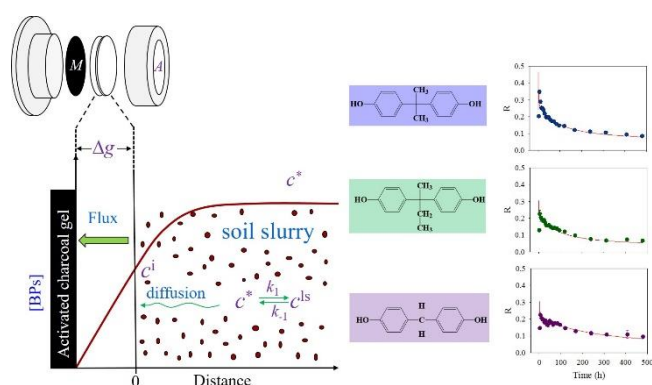
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HIGHLIGHTS

- Desorption/adsorption of BPs in soils affects their mobility and availability.
- Diffusive gradients in thin-films (DGT) was used to assess BPs desorption kinetic.
- DGT was deployed for 2.5 h to 20 d in five soils with different soil properties.
- Poor resupply of BPs from soil solid to solution phase was found.
- Soils with more binding sites could resupply BPs more quickly.

Graphical abstract



For TOC art only

Abstract

Desorption/adsorption of bisphenols (BPs) in soils affects their mobility and availability. However, the kinetics of these processes have not been well studied, due to the lack of appropriate means of measurement. Diffusive gradients in thin-films (DGT) technique can assess kinetic processes in soils and have recently been developed for measuring three BPs (BPA, BPB and BPF). DGT was deployed for 2.5 h to 20 d in five soils with different soil properties. Non-linear increase in mass accumulation by DGT with time indicated poor resupply of BPs from soil solid to solution phase. By

fitting the data with DIFS (DGT-induced fluxes in soils) model, values for the labile partition coefficient (K_{dl}), response time (t_c) and rates of exchange (k_1 and k_{-1}) of BPs between soil solid and solution phases were obtained. The derived values of K_{dl} showed that most of the BPs in the soil could participate in labile exchange. Average response times of 1–2 h implied that the supply of BPs to DGT was limited by their desorption rate. Soils with more binding sites (higher DOM, CEC and Fe oxides) could resupply BPs more quickly, highlighting the danger of just considering partition effects.

Keywords: Bisphenols; Desorption/adsorption; Diffusive gradients in thin-films; DGT-induced fluxes in soils (DIFS); Labile partition coefficient

1. Introduction

Water reclamation and reuse are now considered as key components in the efficient management of water resources [1, 2]. In the United States, in 2006, at least 7.6×10^6 m³ d⁻¹ treated wastewater was reused [3]. Organic contaminants, including BPs, cannot be effectively removed and are commonly detected in the effluents and sludge of sewage treatment plants [4-7]. BPA, the most common BP, is an industrially important chemical widely used for industry [8]. The global demand for BPA was predicted to grow from 6.5 million in 2012 to about 8.3 million tons in 2019 [9]. BPA is an endocrine disrupting chemical and can adversely affect human health [10-12]. BPB and BPF have similar structures to BPA, and can be used as BPA substitutes in industrial applications

[13]. The substantial consumption and emission of BPs inevitably results in them entering into the environment where they react with and are retained by soils, and eventually enter crops. To determine their bioavailability in soils and evaluate their risks to crops, it is necessary to understand the kinetic of their exchange between soil solid and solution phases.

There are several mechanisms which might play a role in the desorption/adsorption of organic chemicals in soils, including ion exchange, interactions with metallic cations, hydrogen bonding, charge transfers, and hydrophobic effects [14]. Therefore, soil properties can greatly influence desorption/adsorption of organic chemicals in soils. For example, there may be ion exchange of cations on negatively charged surfaces of organic chemicals, while pH may determine their main chemical form [15-17]. Desorption/adsorption of many organic chemicals is mainly associated with the organic matter (OM) of the soil, as shown for atrazine [18], tetrabromobisphenol A [19] and polycyclic aromatic hydrocarbons [20]. Although OM content is likely to be crucial, other factors, including Fe oxides [21] content may influence the exchange of organic chemicals between soil solid and solution phases.

Traditionally, the adsorption and desorption of organic compounds in soils have been typically studied using batch equilibrium experiments [22-24]. However, this approach has several disadvantages. Firstly, soils are divided into small subsamples to which target compounds are added. This sub-division introduces the possibility of an inhomogeneous distribution of soil properties affecting the added chemicals. Secondly, in order to determine the chemical concentrations in soil subsamples, it is necessary to

perform extractions using organic solvents followed by solid-phase extraction. Without great care it is easy to introduce errors in such a complex process. Thirdly, with this batch equilibrium test, the rates of chemical exchange between soil solid and solution phases cannot be obtained. These drawbacks can be overcome by using the *in situ* approach of diffusive gradients in thin-films (DGT). DGT is recognized as a useful tool for advancing the understanding of mobility, availability and lability of chemicals in soils and sediments while minimally disturbing soil/sediment structure [25-28]. Moreover, this soil measurement has been shown to be a good predictor of metals and micronutrients in plants [29-31]. DGT introduces a chemical sink within the soil, but does not perturb it in other ways. The magnitude of the flux induced and measured by DGT depends on the diffusion of the chemical in solution and its rate of exchange between solid and solution phases. DIFS (DGT induced fluxes in soils), a dynamic model of the DGT–medium system, can be used to describe quantitatively the exchange of chemicals between solid phase and solution when the soil is perturbed by a DGT device, allowing the acquisition of kinetic parameters for the exchange process [32, 33]. This approach has been used conventionally to obtain information on the desorption kinetics of metals [34-39] and phosphorus [40, 41] in soils. Quite recently, this methodology has been extended to explore the release kinetics of antibiotics from solid phase to solution in soils [42] and municipal biosolids [43]. It was found that the release of the antibiotics from soils or biosolids was generally constrained by slow desorption and diffusion, implying solid phase release kinetics may control the uptake, if fast, of antibiotics by biota [42, 43]. This sheds light on the utilization of DGT to study the

resupply kinetics of other polar organic chemicals, such as BPs, in solid media.

Lately, we reported the development of DGT to measure BPs (BPA, BPB and BPF) in waters using activated charcoal in the binding layer [44]. The aim of this work, as an initial investigation, was to establish the principle of this newly developed technique in obtaining novel information on the exchange kinetics of BPs in soils. Devices were deployed for a wide range of times (2.5 h to 20 d) in 5 diverse soils that had been previously well-equilibrated with three BPs at a level of 2.5 mg kg^{-1} . With the aid of DIFS modeling several kinetics parameters were obtained, including response time, t_c , and the rate constants for dissociation and association, namely k_{-1} and k_1 . Interpretation of how diffusion and exchange processes affected the DGT accumulation was aided by deploying DGT's with different thicknesses of diffusion layer for 24 h.

2. Methods and materials

2.1. Principle of DGT and the DIFS model

The DGT devices were equipped with an agarose-based binding gel containing finely dispersed activated charcoal [44]. The binding gel efficiently traps BPs after they diffuse through an agarose diffusion gel. When the device is deployed in a soil, the continual removal of BPs from the soil solution to the activated charcoal sink induces a concentration gradient within the DGT diffusion layer and immediately adjacent soil (Figure S1). The gradient through the DGT diffusion layer is determined by its thickness, Δg , and the interfacial concentration of labile BPs, c^i , at the DGT–medium interface [45]. According to Fick's first diffusion law (eq. 1), they determine the flux, $J(t)$, of BPs toward the binding gel, where D^s is the diffusion coefficient of BPs in the

diffusive gel. As the BPs accumulate in the DGT, c^i declines. The possible response of the soil to the perturbation exerted by DGT can be considered. If the transport of BPs in soil solution only occurs by diffusion, BPs become depleted in the solution adjacent to the DGT device. This local depletion in concentration may induce chemical desorption from the solid phase. The soil sorption capacity for the BPs and the adsorption/desorption rate determines the effectiveness of this resupply and, consequently, both c^i and the extent to which the depletion extends into the soil solution away from the interface. DGT is therefore best regarded as a robust tool for conducting *in situ* perturbation experiments by introducing a localized sink, rather than as just a simple device for measuring concentrations in the bulk solution of the pore water.

With increasing deployment time, concentrations of BPs in the soil solution become progressively depleted, tending to lower c^i . Therefore, the concentration gradient in the diffusive gel and consequently the flux of BPs towards the activated charcoal gel change with time. The mass per unit area (M_a) of BPs on the binding gel over the deployment time, t , is obtained by integrating the flux over the deployment time (eq 2). The time-integrated interfacial concentration, c_{DGT} , can be calculated by eq 3. After combination of eqs 1–3, c_{DGT} during the deployment time is given as eq 4. Because M_a is the mass per unit area accumulated by DGT, M_a can be expressed as M/A . Here, M is the total mass accumulated in the binding gel and A is the area of the DGT sampling window. Therefore, the time-integrated interfacial concentration or DGT-measured concentration is expressed by eq 5. The ratio, R , of c_{DGT} to the measured soil solution concentration, c^* , is an indicator of the extent of the depletion of soil solution

concentrations at the DGT–medium interface. It depends on the deployment time (eq 5) and is a key measurable parameter that can also be modelled using the DIFS software. c_{DGT} and R are, in effect, integrated measurements, which reflect the variational conditions at the DGT–medium interface over the deployment time.

$$J(t) = D^s \frac{c^i(t)}{\Delta g} \quad (1)$$

$$M_a = \int_{t=0}^t J(t) dt \quad (2)$$

$$c_{DGT} = \frac{\int_{t=0}^t c^i(t) dt}{t} \quad (3)$$

$$c_{DGT} = \frac{M_a \Delta g}{D^s t} \quad (4)$$

$$c_{DGT} = \frac{M \Delta g}{D^s A t} \quad (5)$$

$$R(t) = \frac{c_{DGT}(t)}{c^*} \quad (6)$$

The DIFS model [32] quantifies the dependence of R on the rate and extent of resupply of chemicals from solid phase into solution as well as diffusional supply, both in the soil to the interface and also through the diffusion layer to the sink of the binding layer (Figure S1). Comparison of R measurements from DGT deployments for different times with the DIFS modelled R values allows the estimation of parameters such as the labile distribution coefficient (K_{dl} , see eq 7) of BPs between solid phase and soil solution and the soil response time to depletion (t_c , see eq 8), which is the time needed for the disequilibria of labile BPs induced by DGT to revert to 63% of the equilibrium value [46].

$$K_{\text{dl}} = \frac{c^{\text{ls}}}{c^*} = \frac{k_1}{P_c k_{-1}} \quad (7)$$

$$t_c = \frac{1}{k_{-1} + k_1} = \frac{1}{k_{-1}(1 + K_{\text{dl}} P_c)} \approx \frac{1}{k_{-1} K_{\text{dl}}} \quad (8)$$

The concentration of labile BPs in the solid phase is expressed as c^{ls} , c^* is the concentration of BPs in soil solution, P_c is the particle density [37], k_1 and k_{-1} are the first order rate constant of sorption and desorption, respectively.

The additional measurable parameters required for DIFS fitting are soil porosity (ϕ^s), diffusive gel porosity (ϕ^g) and thickness (Δg), the effective diffusion coefficient in the soil (D^s) and the diffusion gel (D^g), and deployment time (t).

The software 2D_DIFS (version 1.2.3-3, 2005, Lancaster, U.K.) [32], which is available online and runs on a PC with Windows[®] 7, was used to simulate values of K_{dl} , t_c , and the distributions of BPs in solution and solid phases through the DGT–medium system. The parameters of this study are listed in Supplementary data Table S1.

2.2 Soils

Five topsoils (0-20 cm) were sampled from different sites in China: Jilin (JL), Hunan (HN), Jiangxi (JX), Liaoning (LN), Tianjin (TJ). Prior to characterization and experiments, all soil samples were air-dried, passed through a 2-mm sieve to remove roots and stones and to mix soil evenly, and kept in the dark at $25 \pm 1^\circ\text{C}$ for about 1 month. The physicochemical properties of five soils are given in Table 1. Soil pH values in $0.05 \text{ mol L}^{-1} \text{ CaCl}_2$ with soil to solution ratio of 1:5 were determined with a pH meter (Orion Star A214, Thermo Scientific, USA) and electrode (Orion 8102BNUWP, Thermo Scientific, USA). Dissolved organic matter (DOM) in the soils was extracted following a published procedure [47] and measured using a total carbon analyzer (Vario

TOC, Elementar, Germany). Amorphous Fe oxides extracted by ammonium oxalate [48], and total Fe and Mn in the extracts after digestion with HNO₃/H₂O₂, according to USEPA method 3050B, were quantified using flame atomic absorption spectrometry (PinAAcle 900T, PerkinElmer, USA). Particle size analysis was carried out with a laser diffractometer (Mastersizer 2000, Malvern, UK). Maximum water holding capacity (MWHC) was measured by soaking the soil samples in water for 2 h and then draining for 2 h [49]. Cation exchange capacity (CEC) was determined following Sparks et al. (1996) [48].

2.3. Soil amendment

Separate subsamples (2 kg) were amended with a stock solution of BPs to achieve a concentration of 2.5 mg kg⁻¹ for BPA, BPB and BPF. Since microbial activity plays a significant role in the degradation of organic chemicals including BPs [50], sodium azide (NaN₃) was added to inhibit the microbial activity [51]. The amended soils were brought to 50% of MWHC with Milli-Q water (MQ water, Millipore, USA) [39, 42] and left to equilibrate while maintaining soil moisture for 30 d. All soil samples were kept in the dark at 25±1°C.

2.4. DGT preparation and deployment

A standard DGT device consisting of a 0.5-mm thick activated charcoal binding gel, an agarose diffusive gel, a 0.11-mm thick hydrophilic polytetrafluoroethylene (PTFE) filter membrane (0.45 µm) [44] and a plastic holder having an exposure window of 2.51 cm² were prepared according to the standard procedure previously described [44]. The thickness of the diffusive gel was 0.77 mm unless specified in the text.

After aging for 30 d, soils were wetted to 100% MWHC and mixed well to obtain a soil slurry, which was left for 24 h at $25 \pm 1^\circ\text{C}$ prior to DGT measurement [42]. For soil deployment, DGT devices were coated gently with soil paste and then carefully inserted to ensure complete contact with the soil slurry. They were deployed for 2.5, 5, 10, 15, 20, 24, 30, 36, 42, 48, 56, 64, 72, 84, 96, 120, 168, 240, 312, 408, and 480 h at $25 \pm 1^\circ\text{C}$. DGT devices containing agarose diffusive gels of different thickness (0, 0.25, 0.52, 0.77 and 1.29 mm) were also prepared and deployed in the soil slurry for 24 h to investigate the effect of different thicknesses of diffusive layers (diffusive gel + filter membrane) on the uptake of BPs by DGT devices. Three replicates were used. Upon retrieval, DGT devices were jet-washed with MQ water to remove the coherent soil particles. The binding gel was removed and immersed in a mixture of 7 mL methanol + 3 mL 1 mol L^{-1} NaOH for 24 h prior to analysis [44].

After DGT deployment, the soils were centrifuged at $3577 g$ for 15 min to obtain soil solution. Prior to analysis it was filtered into 2 mL glass vials using a 13-mm diameter, $0.45\text{-}\mu\text{m}$ PTFE filter. The soils were then extracted using methanol for analysis of c_s . Little change in the total masses of BPs in the soils indicates there was negligible biodegradation of BPs occurred during the long-term DGT deployment.

DGT-measured concentrations was calculated using Eq 5. BPs samples were measured using high performance liquid chromatography. Detailed information were shown in Supplementary data.

3. Results and discussion

3.1. Concentrations of BPs in soils and their uptake by DGT

Table 2 lists the average concentrations of BPs in soil solution, c^* , and as their methanol-extractable form, c^s , and the percentages of total spiked BPs attributable to c^s after DGT deployment for 2.5–480 h ($n = 21$). Small variances in methanol-extractable BPs in soils and total BPs in soil solution suggest that added sodium azide appeared to inhibit BPs from microbial degradation even for the maximum deployment time of 20-d. The high solubility and low air–water partition coefficient of BPs (Table S2) indicates that they are not volatile at ambient temperatures but have a high tendency for sorption to soil [8]. About half of each of the added BPs were not extractable by methanol solution, indicating that this fraction was tightly bound to the solid phase. This suggestion is supported by the significantly negative correlation of c_s with DOM, CEC, and Fe oxides ($r = -(0.530-545)$, $p < 0.01$, Table S3), which provide binding/exchange sites of BPs in the soil solid phase. Moreover, significantly positive correlation ($r = 0.532$, $p < 0.05$, Table S3) of c^s with soil pH was observed. Therefore, higher soil pH tends to make BPs easier to be extracted by methanol.

Generally, the concentrations of BPs in soil solution in the five soils, c_d , descended in the order: BPA > BPB \approx BPF. The order was similar when concentrations and percentages of the methanol-extractable form were considered; it probably reflects the integrated effect of chemical properties, i.e. octanol–water partition coefficient and acidity constant, of BPs (Table S2). The concentrations of BPs in soil JL were the lowest among the five soils, probably due to it having the highest values of DOM (443 mg L^{-1}), CEC ($24.6 \text{ cmol kg}^{-1}$), and Fe oxides (4.0 g kg^{-1}). Xu et al [50] found that higher Freundlich adsorption coefficients were associated with higher OM content in soils,

indicating that a greater proportion of organic compounds are adsorbed in soils with higher OM, with proportionally lower concentrations in soil solution. The sandy soil HN, with the lowest DOM, MWHC, CEC and Fe oxides (Table 1), had the highest soil solution concentration of BPA and BPF (Table 2). This result is consistent with other reports of organic matter and clay/silt content in soils having the greatest effect on adsorption [52]. However, for BPB, the soil concentration in soil JX was the highest, which can be attributed to the soil's properties. For this soil (JX), although pH (3.99) was the lowest, the total Fe content (18.5 g kg^{-1}) was 1.5-4.6 times than other soils. In this case, the extremely high Fe content (of course together with other soil properties) outweighed pH to become the controlling factor. To some extent, the above mentioned phenomenon are reflected in the correlation analysis, which showed that c_d correlated negatively with CEC ($r = -0.667$, $p < 0.01$, Table S3), amorphous Fe oxides and silt content ($r = -0.569$ and -0.640 , $p < 0.05$, Table S3), while positively with clay content ($r = 0.605$, $p < 0.05$, Table S3).

The dependence of mass accumulation of BPs by DGT on the deployment time is shown in Figure 1. As expected, the DGT-measured mass of each BP increased with increasing deployment time. However, not all the mass–time curves were linear, indicating that resupply from the solid phase to soil solution was insufficient to fully meet the DGT demands and therefore to sustain the initial bulk concentration of soil solution at the DGT–medium interface. For the first 96 h, the order, for each soil, of the DGT-accumulated mass of BPs was consistent with that of soil solution concentrations in the soils, but after 96 h it changed. For example, for the first 96 h, the highest mass

of DGT-accumulated BPA was for soil HN (Figure 1) as it had the highest soil solution concentration. After 96 h, the DGT-accumulated mass in soils JX and TJ gradually surpassed that of soil HN. This trend implies that soil solution provided most of the DGT demand for BPs at the early stage of DGT deployment while at the later stage resupply from the solid phase played the important role in DGT uptake. The relatively large error bars for BPF at long deployment time (> 400 h) was probably caused by the uneven distribution of time-induced BPF hotspots in soils near the DGT sampling window. Further discussion of the resupply of BPs in soils can be found in the following sections.

3.2. Effect of thicknesses of diffusive gels on mass accumulation

Deployment of DGT containing diffusive layers with different thicknesses in the five soils for 24 h was used to inform the nature of the supply of BPs from soil to DGT. The ratio, R , can be used to describe the extent to which resupply from the solid phase maintained the concentration in soil solution [53]. Table S4 lists the change of R value with time, obtained from the ratio of the DGT-measured concentration (c_{DGT}) to the measured initial soil solution concentration (c^*). As expected, the thinner the diffusive layer, the lower the R values. When Δg has the smallest value (0.11 mm), the R values for BPs are the lowest, i.e. 0.03–0.05, indicating limited resupply of BPs from the soil phase. With increasing Δg to 0.36 mm and even higher to 0.63–1.40 mm, the R values increased to 0.09–0.15 and 0.19–0.33, respectively. This reflects increased resupply from soil phase to soil solution, which is eventually captured by the DGT binding layer. The changing trend of R values suggests that thicker gels do induce some limitation of

supply of the available BPs in the soil solution adjacent to the DGT device while the larger demand with the thinner gels may induce a greater limitation in the resupply from the solid phase to solution. Such a limitation in supply from the solid phase may be due to partial exhaustion of the locally available reservoir of BPs or to a kinetic limitation whereby the rate of release from the solid phase cannot keep pace with the demand.

3.3. DIFS modeling for BPs and the kinetics of their exchange

The key experimental information, which can be used to deduce desorption kinetics of BPs from the soil particles to the soil solution, is the change in the measured R values with deployment time (Figure 2). Within a few hours the R values increased steeply to a maximum, and then declined markedly for the next 100 h, followed by a much slower decline. The initial sharp increase in R values is caused by the establishment of a linear diffusion gradient in DGT by BPs diffusing into the diffusive layer in which there was initially no BPs [35]. The consumption of BPs by DGT perturbs their concentration in the immediately adjacent soil. The height of the maximum and the rate of its subsequent decline is influenced by both the desorption rate of BPs from the solid phase in close contact (1–2 mm) with the DGT device and the diffusion of BPs in the soil solution and the diffusive layer. It can be imagined that if the supply is fast enough, i.e. rapid resupply of BPs from an infinite solid phase pool, R values would remain constant. In practice there will always be some finite limit to the resupply caused by the consumption of BPs immediately adjacent to the device and in some cases the desorption rate from the solid phase being too slow to maintain the demand. Consequently, in all cases there is a progressive decline after the maximum. The precise

shape of the declining curve is determined by the capacity of the labile solid phase pool and its rate of release. Modelling this shape allows these terms to be extracted from the data.

Values of the partition coefficient, K_{dl} , and the response time, t_c were obtained by using the DIFS model to optimize their values to give the best fits to the data (Table 3). While K_{dl} and t_c affect the value of R at all times, it is K_{dl} , reflecting pool size, that ultimately controls the amount of BPs that can be resupplied by the soil particles at long time (days); t_c reflects the rate at which BPs are resupplied from the solid phase to soil solution. It primarily influences the magnitude of R at short times (seconds to hours) and consequently the apparent steepness of the early decline [35]. For BPA, the K_{dl} values obtained here were 19–36 mL g⁻¹, which were comparable to previously reported values (1–75 mL g⁻¹) obtained by batch adsorption equilibrium experiments [50, 54]. For the other two BPs, accessible data were not previously reported. There were no significant differences in K_{dl} values among BPs, in consistence with that no significant correlation of K_{dl} values with chemical properties (Table S2) was found (data not shown). By increasing the number of studied chemicals, the relationship between kinetics parameters and chemical properties (such as $\lg K_{ow}$) would probably be found [20]. However, although the values of K_{dl} spanned a quite narrow range, they increased significantly ($r = 0.641\text{--}0.786$, $p < 0.01$, Table S3) with CEC, DOM and silt contents in the soils and with Fe oxides (0.576, $p < 0.05$). This is consistent with these phases encouraging binding of BPs to the solid phase [54, 55].

For BPA, t_c values were in the order of JL < LN < TJ < JX < HN. It indicated that

soil JL could most rapidly respond to a perturbation in the concentration of BPA, whereas soil HN responded most slowly. For the other two BPs, except for one soil, the trend in t_c values was the same as for BPA. Generally, the average t_c values for BPF (107 min) were higher than those for BPA (49 min) and BPB (78 min). All the response times in this study were more than 18 min, with most being in the region of 1 to 2 hours. This slow response indicates that the supply of BPs to the solution phase and hence DGT was limited by the rate of their release from soil solid phase. The only comparative data is for metals and antibiotics. Generally, t_c values for BPs were much higher than those of metals derived from DIFS modeling [35-37]. For Zn and Cd, values are in the range of <1 to 10 min, while for Ni, which is known to desorb slowly, values are no higher than 20 min. The limited data available suggest that antibiotics also desorb slowly ($t_c = 2\text{--}308$ min) [42]. Soils with higher contents of DOM, CEC and Fe oxides appear to resupply BPs more quickly. For soil JL with the highest content of the three parameters, the t_c values were 18, 28 and 60 min for BPA, BPB and BPF, respectively, whereas, for soil HN with the lowest content, the values were accordingly increased to 82, 58 and 179 min respectively. It appears that the nature of the binding sites of BPs in the soil solid phase plays an important role in controlling the resupply of BPs.

Values of k_{-1} and k_1 , which can be derived from K_{dl} and t_c , are rate constants and therefore open to comparison with measurements made by other methods. Few studies have focused on the adsorption and desorption rates of BPs in soils. In a limited study, batch adsorption equilibrium experiments provided values of k_{-1} of $(1.46\text{--}9.85) \times 10^{-6}$ s⁻¹ when the soils were spiked with BPA to levels of 100–1000 $\mu\text{g kg}^{-1}$ [50]. The k_1

values obtained in this study (Table 3) using DGT-DIFS had similar values, ranging from $(2.3\text{--}14) \times 10^{-6} \text{ s}^{-1}$, generally following the order $\text{BPA} > \text{BPB} > \text{BPF}$. We could not find any reported values of k_{-1} for BPB and BPF. In accordance with eq 8, k_{-1} is negatively correlated with t_c (Table S3). Consequently, k_1 correlates positively with DOM ($r = 0.687$, $p < 0.01$, Table S3) and, a little less significantly with CEC ($r = 0.616$, $p < 0.05$, Table S3).

In principle, DGT technique can be used to obtain chemical desorption information in field soils, for which, concentration of BP in soil solution will be lowered when there is ingress of water from precipitation or surface flow. The findings of this work suggest that most BPs will ultimately leach from soils with reasonable water flow, but the rate of leaching can be expected to be substantially slower than that of readily exchangeable ions. Another mechanism that can locally lower the concentration of solution components is their uptake by plant roots. Work with metals has shown that uptake by DGT mimics some aspects of plant uptake. Where uptake by plants is quite rapid the concentration in the immediately adjacent solution can be lowered, as for DGT. The relatively slow release of BPs from the solid phase suggests that it will limit the rate at which they can be taken up by plants.

4. Conclusions

This study established the methodology for investigating, in a low-disturbance way, the kinetics of BPs desorbed from soils. It has shown that, for the soils studied, most of the BPs (BPA, BPB or BPF) can be released into solution if the equilibrium concentration in solution is lowered. That is because the BPs are generally not fixed in

an inert form in the soils. The rate of release is relatively slow. BPs are not instantaneously released in response to perturbation of the solution concentration. Rather, a period of 1 to 2 hours is required to approach the new equilibrium state. These conclusions apply to all studied BPs, but BPA had the most rapid response and BPF the slowest. Phases expected to bind BPs, namely OM, Fe oxides and silt, had the highest K_{dl} values, but the lowest values of t_c . This highlights the danger of just considering partition effects. Although a greater proportion of the BPs were bound to the solid phase in these soils they were more kinetically available for release.

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Appendix A. Supplementary data

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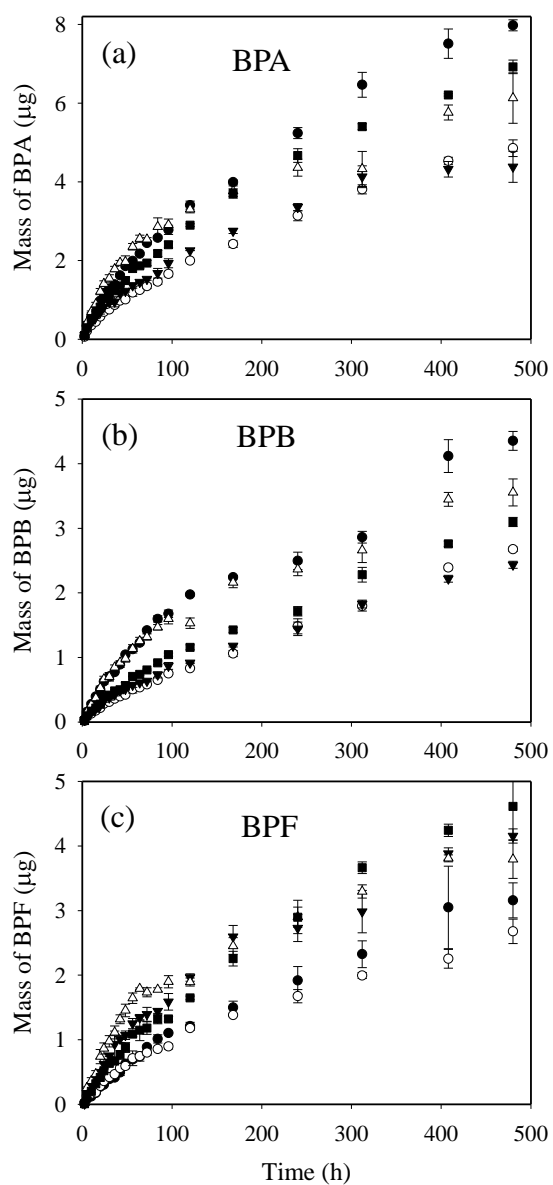


Figure 1. Dependence of the accumulated masses of BPA, BPB and BPF in the binding gel from DGT deployment in five soils on the deployment time. ●, ○, ▼, △, and ■ represent soils JX, JL, LN, HN and TJ, respectively. Error bars are calculated from the standard deviation of three replicates.

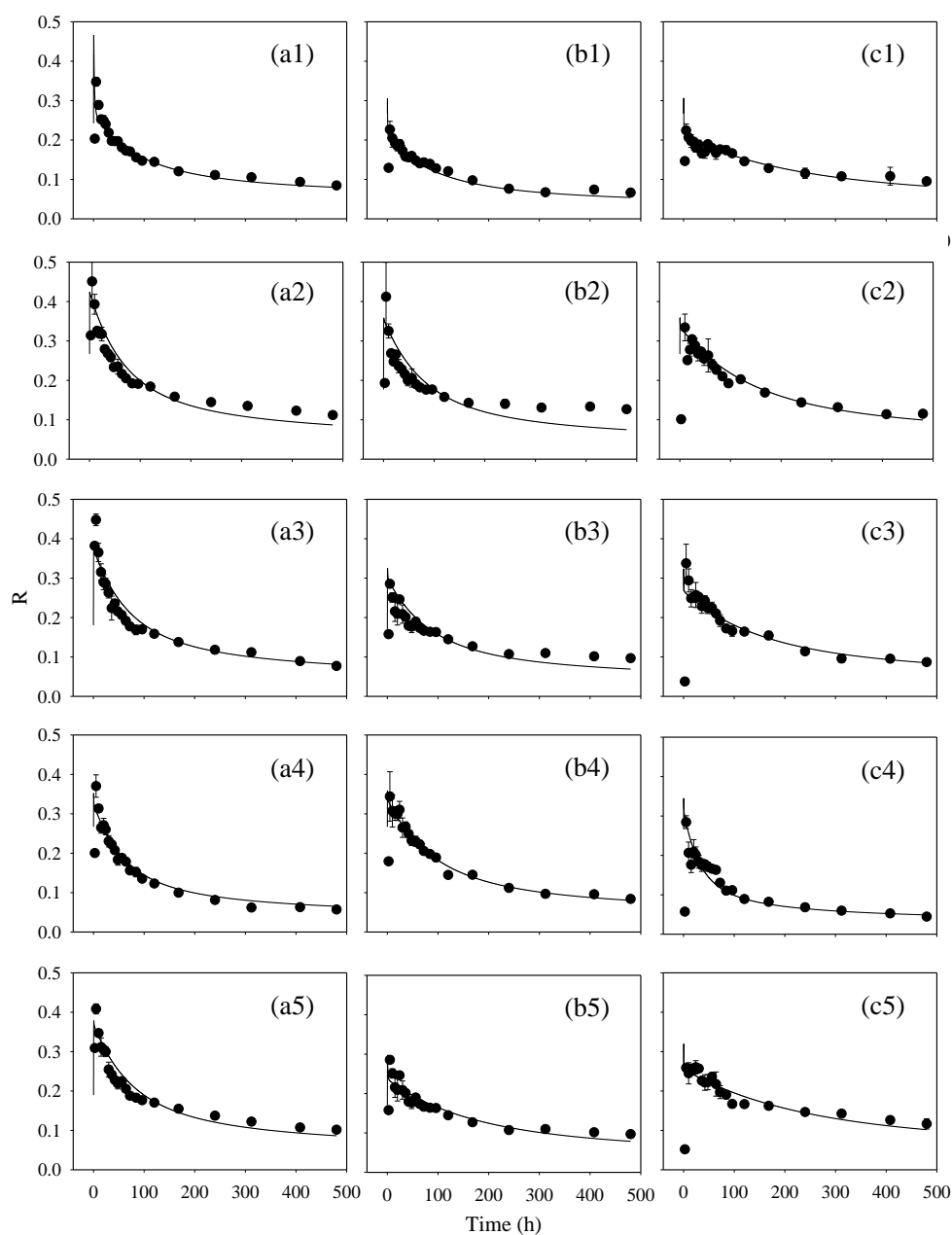


Figure 2. Dependence of measured R values for BPA (a1–a5), BPB (b1–b5) and BPF (c1–c5) in five soils on deployment time. The line shows the best fit using the 2D_DIFS model. The symbols in each figure from left to right correspond to deployment time of 2.5, 5, 10, 15, 20, 24, 30, 36, 42, 48, 56, 64, 72, 84, 96, 120, 168, 240, 312, 408, and 480 h, respectively. Letters a, b and c stand for BPA, BPB and BPF, respectively, and numbers 1, 2, 3, 4 and 5 represent soils JX, JL, LN, HN and TJ, respectively. Error bars are calculated from the standard deviation of three replicates.

Table 1. Physical and chemical properties of the five soils.

Soils	JX	JL	LN	HN	TJ
pH	3.99	5.45	6.40	7.50	7.90
MWHC (%) ^a	52.3	56.3	45.7	37.0	64.5
DOM (mg L ⁻¹) ^b	74.7	443	110	47.9	58.1
CEC (cmol kg ⁻¹) ^c	9.18	24.6	13.7	4.16	17.1
Total Fe (g kg ⁻¹)	18.5	4.63	5.08	3.30	7.50
Amorphous Fe oxides (g kg ⁻¹)	3.34	4.00	2.46	1.19	3.56
Total Mn (g kg ⁻¹)	0.05	0.36	0.37	0.30	0.17
Particle size (%)					
Clay (<2 μm)	18.2	14.6	8.6	4.7	18.4
Silt (2-50 μm)	64.4	74.2	77.2	40.1	78.4
Sand (>50 μm)	17.4	11.2	14.2	55.2	3.3

^a maximum water holding capacity.

^b dissolved organic matter.

^c cation exchange capacity.

Table 2. Concentrations (mean \pm SD, $n = 21$) of BPs in soil solution, c^* , extractable BPs, c^s , by methanol in soils including its percentages to total spiked BPs.

soils	BPA			BPB			BPF		
	c^* ($\mu\text{g L}^{-1}$)	c^s (mg kg^{-1})	% of c^s	c^* ($\mu\text{g L}^{-1}$)	c^s (mg kg^{-1})	% of c^s	c^* ($\mu\text{g L}^{-1}$)	c^s (mg kg^{-1})	% of c^s
JX	333 \pm 46.9	1.33 \pm 0.08	53 \pm 3	278 \pm 20.0	1.25 \pm 0.08	50 \pm 3	111 \pm 7.5	1.25 \pm 0.08	50 \pm 3
JL	175 \pm 15.7	1.03 \pm 0.08	41 \pm 3	102 \pm 13.2	0.95 \pm 0.08	38 \pm 3	77.4 \pm 7.4	0.95 \pm 0.05	38 \pm 2
LN	234 \pm 13.2	1.38 \pm 0.05	55 \pm 2	114 \pm 13.6	1.20 \pm 0.03	48 \pm 1	159 \pm 16.7	1.20 \pm 0.08	48 \pm 3
HN	450 \pm 52.6	1.45 \pm 0.10	58 \pm 4	228 \pm 55.2	1.48 \pm 0.10	59 \pm 4	296 \pm 48.6	1.48 \pm 0.10	59 \pm 4
TJ	268 \pm 13.8	1.50 \pm 0.10	60 \pm 4	143 \pm 12.6	1.38 \pm 0.13	55 \pm 5	129 \pm 9.8	1.30 \pm 0.10	52 \pm 4

Table 3. Parameters for BPA, BPB and BPF in five soils derived from model fits using 2D_DIFS. The units of K_{dl} , t_c , k_{-1} and k_1 are mL g^{-1} , 10^3 s , 10^{-6} s^{-1} and 10^{-5} s^{-1} , respectively.

Soils	BPA				BPB				BPF			
	K_{dl}^a	t_c^b	k_{-1}^c	k_1^d	K_{dl}	t_c	k_{-1}	k_1	K_{dl}	t_c	k_{-1}	k_1
JX	25	4.4	4.6	22	26	8.7	2.3	11	26	5.7	3.5	17
JL	36	1.1	14	92	49	1.7	6.7	58	52	3.6	2.9	27
LN	29	2.0	7.8	50	45	3.7	2.7	27	42	4.6	2.3	21
HN	19	4.9	3.9	20	29	3.5	3.6	29	11	10.7	2.9	9
TJ	28	2.2	9.9	43	42	5.7	2.7	17	32	7.6	2.6	13

^a distribution coefficient of labile analyte between solid phase and soil solution.

^b soil response time to depletion, which is the time needed for the disequilibria of labile analyte induced by DGT to revert to 63% of the equilibrium value.

^c first order desorption rate constant.

^d first order sorption rate constant.