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ARTICLE *in* ENVIRONMENTAL SCIENCE & TECHNOLOGY · APRIL 2014

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Desorption Kinetics of Sulfonamide and Trimethoprim Antibiotics in Soils Assessed with Diffusive Gradients in Thin-Films

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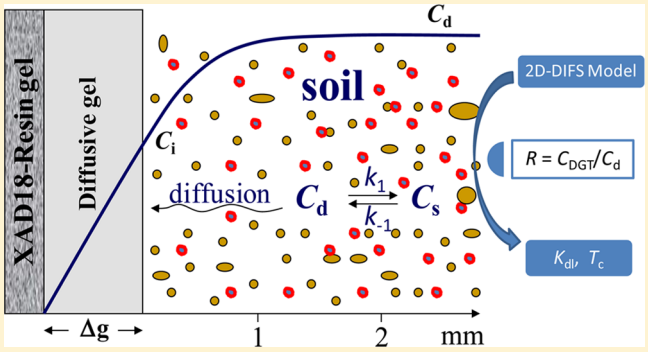
Supporting Information

ABSTRACT: Although sorption/desorption of antibiotics in soils affects their mobility and availability, with consequences for risks to the surrounding environment, the dynamics of these processes are not well-known. In this study, diffusive gradients in thin-films devices suitable for measuring polar organic compounds (o-DGT) were deployed in two soils for a range of times (5 h to 20 d) to measure the distribution and rates of exchange between solid phase and solution of three sulphonamides (SAs; sulfamethoxazole, SMX; sulfamethazine, SMZ; and sulfadimethoxine, SDM) and trimethoprim (TMP). o-DGT continuously removes antibiotics to a XAD gel layer after passage through a well-defined diffusion layer and therefore perturbs their concentration in the adjacent soil solution. This induces a remobilization flux from the solid phase, which is related to the concentration of antibiotics in the soil solution, their diffusional supply, and the exchange kinetics between dissolved and sorbed antibiotics. A dynamic model of solute interactions called DIFS (DGT induced fluxes in soils) was used to derive distribution coefficients for labile antibiotics (K_{dl}) and the rate constant for supply of antibiotics from solid phase to solution, expressed as a response time (T_c). Larger labile solid phase pools were observed for TMP than for SAs. The soils could resupply TMP so rapidly that in one soil, where T_c = 2 min, supply was controlled by diffusion. Response times for SAs were generally longer (>27 min), particularly for SDM (>3 h), implying that the supply of SAs to o-DGT samplers was limited by the desorption release rate. A wider implication of this study is that similar solid phase release kinetics may control the uptake of antibiotics by biota.



INTRODUCTION

Fate and transport of the emerging pollutants known as PPCPs (pharmaceuticals and personal care products)[1] in the soil environment depends largely on their interaction (sorption/desorption) with the soil solids. Understanding contaminant sorption and desorption in the environment is essential to determine their bioavailability, predict their fate and transport, and assess risks.

Antibiotics are one of the most important classes of PPCPs that are widely administered to humans and animals.[2] They can enter the soil system through irrigation practices and manure or sludge applications.[3−5] Most studies have focused on their equilibrium partitioning in soil. There has been less emphasis on the kinetic aspects of antibiotic exchange, but there is increasing recognition of potential kinetic controls on contaminate supply in soils.[6] Rates of reactions of organic chemical in soil are frequently assessed using batch or dynamic column experiments[7−9] or are followed by isotopic exchange methods.[10,11] An alternative passive sampling approach, o-DGT (diffusive gradients in thin-films, DGT, for organics),[12] has been proposed recently for measuring the dynamics of antibiotics with minimal disturbance to the soil (unpublished results). This initial study using o-DGT was useful in advancing understanding of the mobility and availability of antibiotics in soil, but the extent to which the supply of antibiotics by the solid phase is kinetically limited was not fully answered.

A dynamic model of the DGT−soil system (DIFS, DGT induced fluxes in soils)[13,14] that describes the diffusional transport and dynamic exchange of solute between solid phase and solution when a soil is perturbed by a DGT device can be used to obtain kinetic and pool size parameters of the soil from the DGT measurements. We adopted this DIFS model, which had been initially used to describe the dynamics of metal exchange, to interpret o-DGT measurements of antibiotics in soils in terms of kinetic and partitioning parameters. The o-DGT samplers were deployed in aged soils for different time periods, and models (DIFS) of the dependence of the accumulated antibiotics on time were used to provide estimates

Received: January 13, 2014
Revised: March 28, 2014
Accepted: April 4, 2014
Published: April 4, 2014

of desorption rate constants and the pool size of labile antibiotics in the solid phase.

METHODS AND MATERIALS

Principles of o-DGT and the DIFS Model. o-DGT employs XAD18 resin as the binding agent in an agarose receiving gel. The material diffusion layer comprises an agarose diffusion gel and a filter membrane. Analyte diffuses through the diffusion layer and then is trapped in the resin gel. After an initial approach to steady state, there is a linear concentration gradient in the diffusive gel layer (Figure 1). The gradient

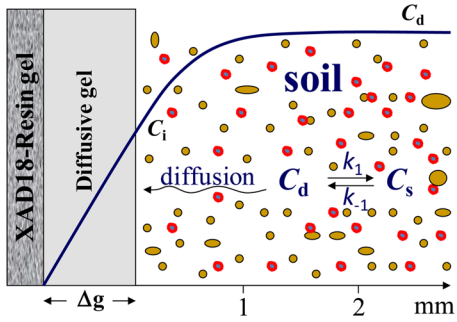


Figure 1. Processes involved in the o-DGT−soil system induced by deployment of o-DGT in soil. Analyte is accumulated by diffusion across the diffusion layer (thickness, Δg, cm). Lowering of the soil solution concentration of analyte (C_d) will induce desorption (with a rate constant k_{-1}) from the soil particles (with concentration of labile analyte of C_s). k_1 is the sorption rate constant; C_i is the instantaneous concentration at the interface between o-DGT and the soil solution.

depends on the thickness of the diffusion layer, Δg, and the interfacial concentration of labile antibiotics, C_i. According to Fick's first law (eq 1), the instantaneous flux, $F(t)$, toward the resin-gel is determined by C_i. D_d is the diffusion coefficient of the labile antibiotic in the diffusion layer (values for each antibiotic are given in the section Calculation of Concentration from o-DGT). As the antibiotic is consumed by o-DGT, its interfacial concentration, C_i, declines, which induces a flux of antibiotics from the soil solid phase to solution, which contributes to the flux to the o-DGT. The soil sorption capacity for the antibiotic and the rate of the adsorption and desorption processes determine the extent of the resupply and consequently both C_i and the extent to which the depletion extends into the soil solution away from the interface. Inevitably, as the antibiotics are taken up by the o-DGT the amount of antibiotics in the depletion zone is consumed. Consequently, the rate of supply will diminish with time, and C_i will progressively decline.

The total mass (M) of antibiotics accumulated, over the deployment time, T, is given by integrating the flux over the deployment time (eq 2). Then the time averaged interfacial concentration, C_{DGT}, can be calculated (using eq 3) from M, which can be measured by high performance liquid chromatography (HPLC)−mass spectrometry (MS) or UV after extracting the antibiotic from the binding gel. The exposed area of the diffusion layer is A. The ratio, R, of C_{DGT} to the independently measured initial soil solution concentration, C_d, is an indicator of the extent of the depletion of soil solution concentrations at the o-DGT interface. It depends on the deployment time (eq 4) and is a key measurable parameter in the DIFS model.

$$F(t) = \frac{D_d C_i(t)}{\Delta g} \quad (1)$$

$$M = \int_0^T F(t)\, dt \quad (2)$$

$$C_{DGT} = \frac{M\Delta g}{D_d A T} \quad (3)$$

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

The DIFS model[15] quantifies the dependence of R on resupply of analyte from solid phase to solution coupled to diffusional supply both in the soil to the interface and also through the diffusion layer to the assumed instantaneous and infinite sink of the resin gel.[14−16] It uses K_{dl}, the distribution coefficient of labile analyte (eq 5) and the response time, T_c (eq 6), to describe the kinetics of adsorption (rate constant, k_1) and desorption (rate constant, k_{-1}). K_{dl} may be lower than the corresponding value of K_d that is based on the total analyte measured in the soil. T_c is the characteristic time for the system to approach equilibrium.[17]

$$K_{dl} = \frac{C_s}{C_d} = \frac{k_1}{P_c k_{-1}} \quad (5)$$

$$T_c = \frac{1}{k_{-1} + k_1} = \frac{1}{k_{-1}(1 + K_{dl}P_c)} \quad (6)$$

Depending on its mode of operation, DIFS can be used to calculate R from inputs of K_{dl} and T_c, or model fits of R versus time can be used to derive estimates of K_{dl} and T_c. Irrespective of the operation mode, DIFS provides the concentrations of solution and solid-phase analyte concentrations spatially and temporally within the o-DGT-soil system.

The software 2D_DIFS (version 1.2.3-3, 2005, Lancaster, U.K.) was used to obtain values of K_{dl} and T_c, and 1D_DIFS (1999, Lancaster, U.K.) was used for simulation of the distributions of analytes in solution and solid phases. They are freely available online[18] and run on a PC with windows 7 OS (professional, 32 bit). The key parameters are listed in Supporting Information Table S1.

Chemicals. Four antibiotics, sulfamethoxazole (SMX, purity >98%), sulfamethazine (SMZ, purity >99%), sulfadimethoxine (SDM, purity >98.5%), and trimethoprim (TMP, purity >99%), and $^{13}C_3$-caffeine (^{13}C-CAF as the internal standard, purity >99%) were all purchased from Sigma-Aldrich (Poole, U.K.). Their physiochemical properties are given in Supporting Information Table S2.

Antibiotic stock solutions were dissolved in pure methanol. Acetonitrile (ACN) and methanol (MeOH) were purchased from Fisher (Poole, U.K.). Sodium Azide (NaN_3) was purchased from Sigma-Aldrich (Poole, U.K.).

Soils. The soils characterized as stagnogley soil (A) and brown-earth soil (B) were collected from two sites in Lancashire, U.K. The physicochemical properties of each soil are A, clay loam, sand 56%, silt 25%, clay 19%, pH(dH_2O) 6.5, pH($CaCl_2$) 5.2, maximum water holding capacity (MWHC) 46%, soil organic matter (SOM) 4.8%; B, sand 55%, silt 27%, clay 18%, pH(dH_2O) 5.4, pH($CaCl_2$) 5.0, MWHC 51%, SOM 9.3%. The soils were air-dried and passed through a 2 mm sieve to remove roots and stones prior to experiments.

dx.doi.org/10.1021/es500194f | Environ. Sci. Technol. 2014, 48, 5530−5536

Table 1. Concentrations (mean ± SD, n = 15) of Antibiotics in Soil Solution (C_d) and Extractable by Acetonitrile (C_s)

soils		TMP	SMZ	SMX	SDM
A	C_d (ng/mL)	54 ± 7.8	739 ± 129	1511 ± 363	582 ± 136
	C_s (ng/g)	759 ± 61	903 ± 115	916 ± 116	761 ± 150
B	C_d (ng/mL)	85 ± 12	558 ± 80	1118 ± 171	332 ± 78
	C_s (ng/g)	1281 ± 41	743 ± 67	841 ± 56	691 ± 77

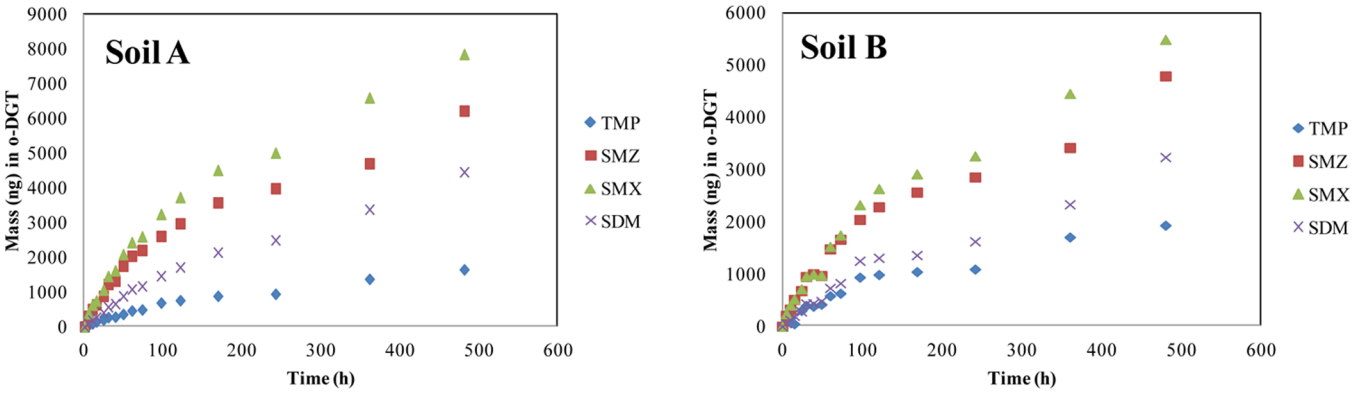


Figure 2. Dependence on deployment times of the accumulated masses of antibiotics from o-DGT deployments in soils A and B.

Soil Spiking and Preparation. Antibiotic standards prepared in methanol were spiked into soils to deliver individual antibiotic concentrations of 2.5 mg kg^{-1}. NaN_3 was added to inhibit the microbial activity.[7] To minimize solvent effects, the antibiotic standards were first added to 25% of the used soil and allowed to vent before addition of the remaining soil.[19] Blank soils that were not augmented with antibiotics were also prepared. The soils were then wetted to 50% MWHC by adding appropriate amount of high purity water (MQ water) (Milli-Q water system, U.K.), mixing well, and leaving for 15 days. After aging, soils were wetted to 100% MWHC and mixed well to obtain a soil slurry, which was left for 24 h at room temperature prior to deployment of o-DGT. The particle concentration (P_c) and the porosity of soil (ϕ_s) are given in Table S1 in Supporting Information, assuming a standard particle density of 2.65 g/mL.

o-DGT Preparation and Deployment. Standard o-DGT devices with 0.5 mm XAD18 resin gels, 0.8 mm agarose diffusive gels, and 0.14 mm polyethersulfone filter membranes were prepared as in described previously.[12] For deployment in the soil, o-DGT devices were rinsed with MQ water, soil paste was smeared gently onto the filter surface by hand, and then the device was pressed firmly on the soil to ensure a good contact between the soil and the o-DGT unit. o-DGT devices were deployed for 5, 10, 15, 24, 30, 39, 49, 60, 73, 97, 121, 169, 242, 361, and 481 h in the laboratory at room temperature, 16 ± 3 °C.

o-DGT Retrieval and Soil Sampling. After deployment, o-DGT devices were retrieved, and the filter surface was jet washed with MQ water. The binding gel was removed and put into 15 mL amber glass vials. Five milliliters of MeOH was added, and the vials placed in an ultrasonic bath for 20 min, which resulted in >95% elution recovery according to our previous study.[12]

After retrieving o-DGT, the soils were stirred, and about 5 g of soil was sampled and centrifuged at 3000 rpm for 30 min to obtain soil solution, which was filtered (with a 0.2 μm PP syringe filter, Pall, U.K.) into 1 mL glass vials prior to analysis for C_d. The soils were then extracted using acetonitrile for analysis of C_s, The ratio, K_d, was calculated from C_s/C_d. All samples were dissolved in an initial mobile phases prior to analysis by HPLC−UV or HPLC−MS.

Chemical Analysis. All samples were analyzed for antibiotics by HPLC−UV (see Supporting Information). The soil solution samples were also analyzed by HPLC−MS following the previous method.[20] Details are given in the Supporting Information.

Calculation of Concentration from o-DGT. Equation 3 was used to calculate the averaged concentration of antibiotics at the interface (C_{DGT}). The D_d values for TMP, SMZ, SMX, and SDM at 16 °C were 2.93 × 10^{-6}, 3.10 × 10^{-6}, 3.95 × 10^{-6}, and 2.97 × 10^{-6} cm^2 s^{-1}, respectively, according to previous study.[20]

RESULTS AND DISCUSSION

Distributions in Soils. The concentrations in soil solution (C_d) and solid phase (C_s) did not change appreciably (p > 0.05) after 2 weeks of aging. The concentrations in the soil solution and in the soil particles extracted by acetonitrile are given in Table 1. The nonextractable antibiotics were 70%, 64%, 63%, and 70% for TMP, SMZ, SMX and SDM, respectively, in soil A and were 49%, 70%, 66%, and 72% in soil B.

The concentrations of antibiotics in the soil solution had the same order for both soils: SMX > SMZ > SDM > TMP. Both C_d and C_s of the three sulphonamide antibiotics (SAs) were less in soil B than in soil A, while for TMP they were higher in soil B than in soil A. The observations for sulphonamides are consistent with previous studies,[21] which found that higher SOM and lower pH will suppress the desorption of SAs from soil and consequently lead to lower soil solution concentrations. The enhanced solubility of TMP in soil B is consistent with our previous observation of an enhanced flux of TMP from soil to solution when SOM was added to a soil (unpublished results). It appears that the equilibrium states of SAs and TMP are quite different in soils. TMP is characterized by a higher K_d and lower C_d than SAs.[22] Their kinetics of desorption will be addressed in the later sections.

dx.doi.org/10.1021/es500194f | Environ. Sci. Technol. 2014, 48, 5530−5536

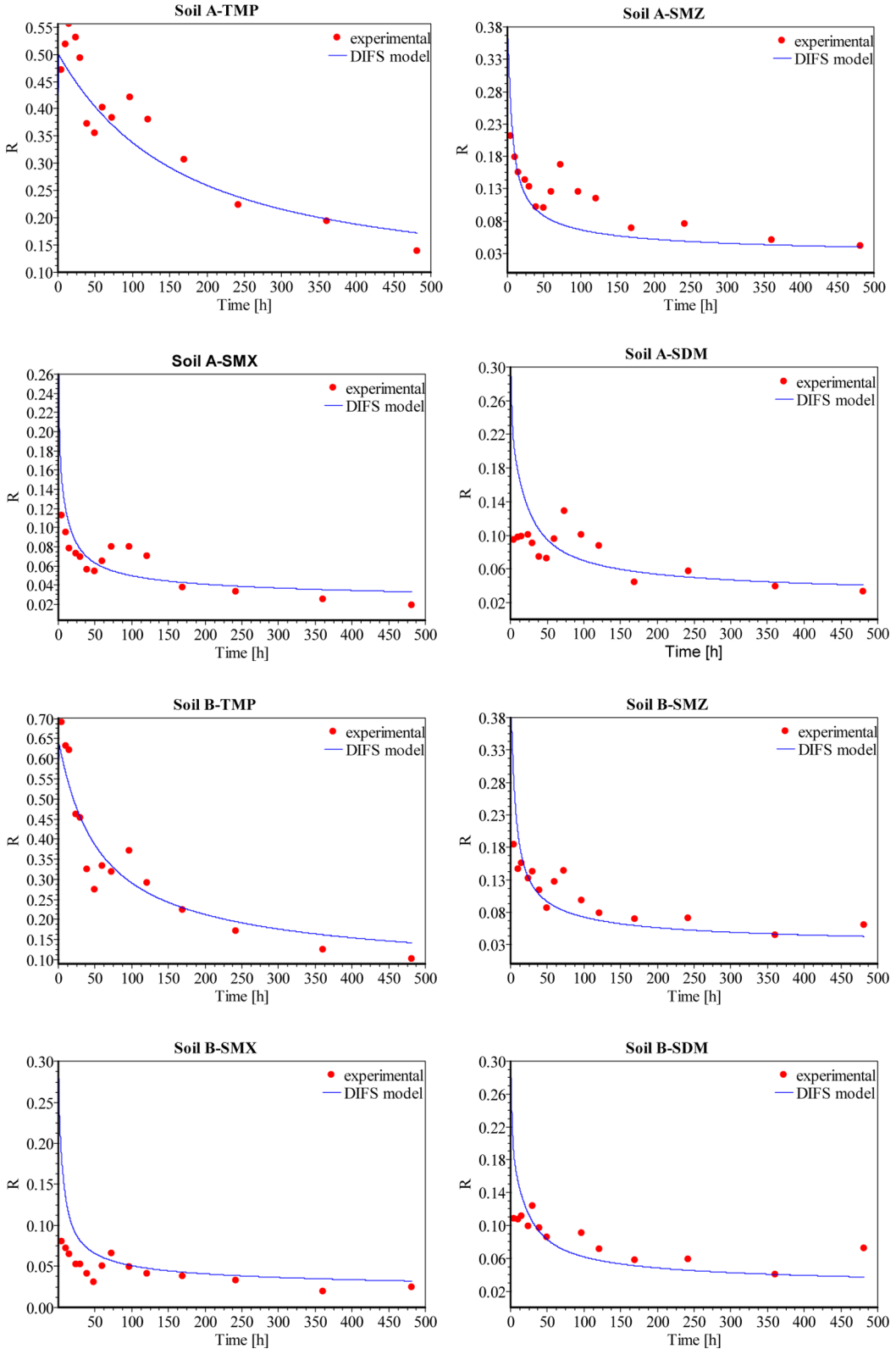


Figure 3. Dependence of measured values of *R* for TMP, SMZ, SMX, and SDM in soils A and B on deployment time. The lines show the best fits using the 2D_DIFS model.

Uptake of Antibiotics by o-DGT. The mass of each antibiotic accumulated in the o-DGT increased with deployment time (Figure 2). The nonlinearity of the mass−time curve implies that, for both soils, the supply from solid phase to solution could not sustain fully the DGT demand. At any given time, the mass of antibiotics accumulated were in the order SMX > SMZ > SDM > TMP for both soils, which is consistent with the order of solution concentrations of these antibiotics. The extent to which the mass accumulated in the o-DGT deviated from the theoretical linear line for the fully sustained

dx.doi.org/10.1021/es500194f | *Environ. Sci. Technol.* 2014, 48, 5530−5536

case will depend on size of the labile pool of antibiotics in the solid phase and the rate of the resupply to solution, as explored in the next section.

DIFS Modeling for Antibiotics. To obtain information on the kinetics of desorption from the soil particles to the soil solution of these antibiotics, experimental data were fitted using the DIFS model. The measured ratio, R, was plotted against deployment time (Figure 3) for each antibiotic in each soil. The general trend is an initial steep decline in R followed by a slower decline that in some cases approaches a constant value. Theoretically there should be an initial increase in R, attributable to the establishment of a linear diffusion gradient in the diffusion layer, which is initially free from antibiotics, but this occurs too quickly to be observed on the measured time scale (first data point at 5 h).[13] If there was a very rapid supply from the solid phase, which had an infinite concentration of labile antibiotic, R would be constant after its initial increase. The decline reflects the gradual decline in the concentration of antibiotics in the solution at the sampler interface, as they are removed to the DGT binding phase more quickly than they can be supplied by diffusion and release from the solid phase. For both soils, the largest R values were observed for TMP, followed by SMZ > SDM ≥ SMX, implying that the ability of the soils to sustain initially the original soil solution concentrations decreased in the same order.

Best fits of the plots of R versus deployment time were obtained by using the 2D_DIFS model and optimizing the values of the response time, T_c, and the partition coefficient for each labile antibiotic, K_{dl}.[15] The values of K_{dl} and T_c, along with the derived values of the association and dissociation rate constants, are presented in Table 2 for each soil. As for the comparison of most models with experimental data, the fits are not perfect with apparent systematic deviations being most prevalent for t < 20 h. While this may reflect experimental issues, it most likely indicates that the model used does not adequately simulate all processes. For example, the possibility of multiple pools of adsorption sites characterized by different sorption kinetics has been proposed. Therefore, derived parameters, such as K_{dl}, will provide only a summary assessment.

Table 2. Parameters for TMP, SMZ, SMX and SDM in Soils A and B Derived from Model Fits Using 2D_DIFS

soil	parameter	TMP	SMZ	SMX	SDM
A	K_d ACN[a] (mL/g)	15	1.3	0.68	1.5
	K_{dl} o-DGT (mL/g)	74	1.4	0.54	0.41
	T_c (s)	1091	1847	13 244	18 465
	k_1 (10^{-5} s^{-1})	91	41	4.0	2.5
	k_{-1} (10^{-6} s^{-1})	5.9	135	35	29
B	K_d ACN[a] (mL/g)	16	1.3	0.78	2.3
	K_{dl} o-DGT (mL/g)	50	1.8	0.80	1.0
	T_c (s)	127	1636	4864	14 179
	k_1 (10^{-5} s^{-1})	780	48	13	48
	k_{-1} (10^{-6} s^{-1})	74	126	77	228

[a]Values of K_d obtained by acetonitrile (ACN) extract.

Labile Pool Size. An estimate of K_d was obtained by measuring the concentration of each antibiotic released by ACN extraction (Table 2). The K_{dl} values for TMP determined by o-DGT were higher for both soils (by a factor of 3−5, p < 0.05) than the K_d obtained by ACN extraction, whereas the o-DGT derived K_{dl} values for SMZ and SMX and SDM were close to the values determined by ACN extraction. The agreement of the o-DGT and ACN extraction measurements for SAs suggests that the two approaches access similar solid phase pools. The appreciable difference between these two methods for TMP is puzzling. To contribute to a DGT measurement, the antibiotics in the labile solid phase pool must dissociate on a time scale of several minutes.[13] It appears that some TMP can be rapidly released if the concentration in solution is lowered, and yet it fails to dissolve in ACN. Such rapid release is consistent with the importance of ionic interactions between TMP and soil components such as clay minerals. The results indicate that whereas the ACN extraction method could serve as a simple and quick approach to assess the availability of the SAs, it would underestimate the availability of TMP in soil. The higher K_{dl} obtained for TMP than for SAs demonstrates that there is a greater reservoir of labile TMP for potential resupply to soil solution.

Kinetics of Antibiotic Exchange. Whereas K_{dl} ultimately controls the magnitude of the amount of antibiotic that can be resupplied by the soil particles, T_c and k_{-1} relate directly to how fast the solid phase can resupply the concentration in soil solution.[17] T_c primarily influences the magnitude of R at short times and consequently the apparent steepness of the early decline in the model fits of R versus time (Figure 3).[13] For a given value of K_{dl} there will be a limiting value of T_c (T_c^0), below which T_c has a negligible effect on R because desorption kinetics no longer limit the rate of supply. The resupply then depends solely on the pool size of labile antibiotics and diffusional transport.

In both soils, T_c values for these antibiotics were in the order SDM > SMX > SMZ > TMP, indicating that TMP (18 and 2 min for soil A and B, respectively) can be supplied most rapidly to the solution phase. For TMP, lowering T_c by an order of magnitude results in about a 20% increase in R for soil A (for 15 h deployment) but only up to ∼4% for soil B (for 1 h deployment). Therefore, the diffusion-limiting case is effectively reached for TMP in soil B, but for soil A, there is some kinetic limitation. However, the same order of decrease of T_c raised the value of R for SAs by 14−38% in both soils at very short time (<5 h), but only by <10% at longer times. This suggested that for the supply of SAs is partly limited kinetically in both soils at short deployment times, while for longer deployment times it is limited by diffusion and potential depletion of the solid phase reservoir. For all four antibiotics, T_c values in soil A appears to be higher than that in soil B, but the difference is most marked for TMP and SMX. Given the similar soil texture, this suggests that the soil properties of SOM (soil A < soil B) and/or pH (soil A > soil B) may influence the solid phase release kinetics of both TMP and SAs.

The sorption of antibiotics in soils is well documented in the literature,[3−5,7,8,21,23−27] including sorption kinetics for SAs, with k_1 ranging from 1.1 × 10^{-8} to 143 × 10^{-5} s^{-1},[3,4,8] which embraces our values. There is lack of k_{-1} values for these antibiotics in soils. Several studies investigated another SA, sulfadiazine, and derived k_{-1} at 5.2 × 10^{-8} s^{-1} and 7.1 × 10^{-8} s^{-1},[28] 8.0 × 10^{-7} to 8.2 × 10^{-7} s^{-1},[8] and 1.1 × 10^{-6} s^{-1}.[3] These values are smaller than our values in this study (Table 2), which is reasonable considering the fact that o-DGT acts as an infinite sink for the compounds, and only partial release is required in obtaining the DGT data.

DIFS can help appreciate the effect of capacity and kinetic factors on the transport of analytes in the o-DGT−soil system. The simulated profiles of dissolved and sorbed concentrations

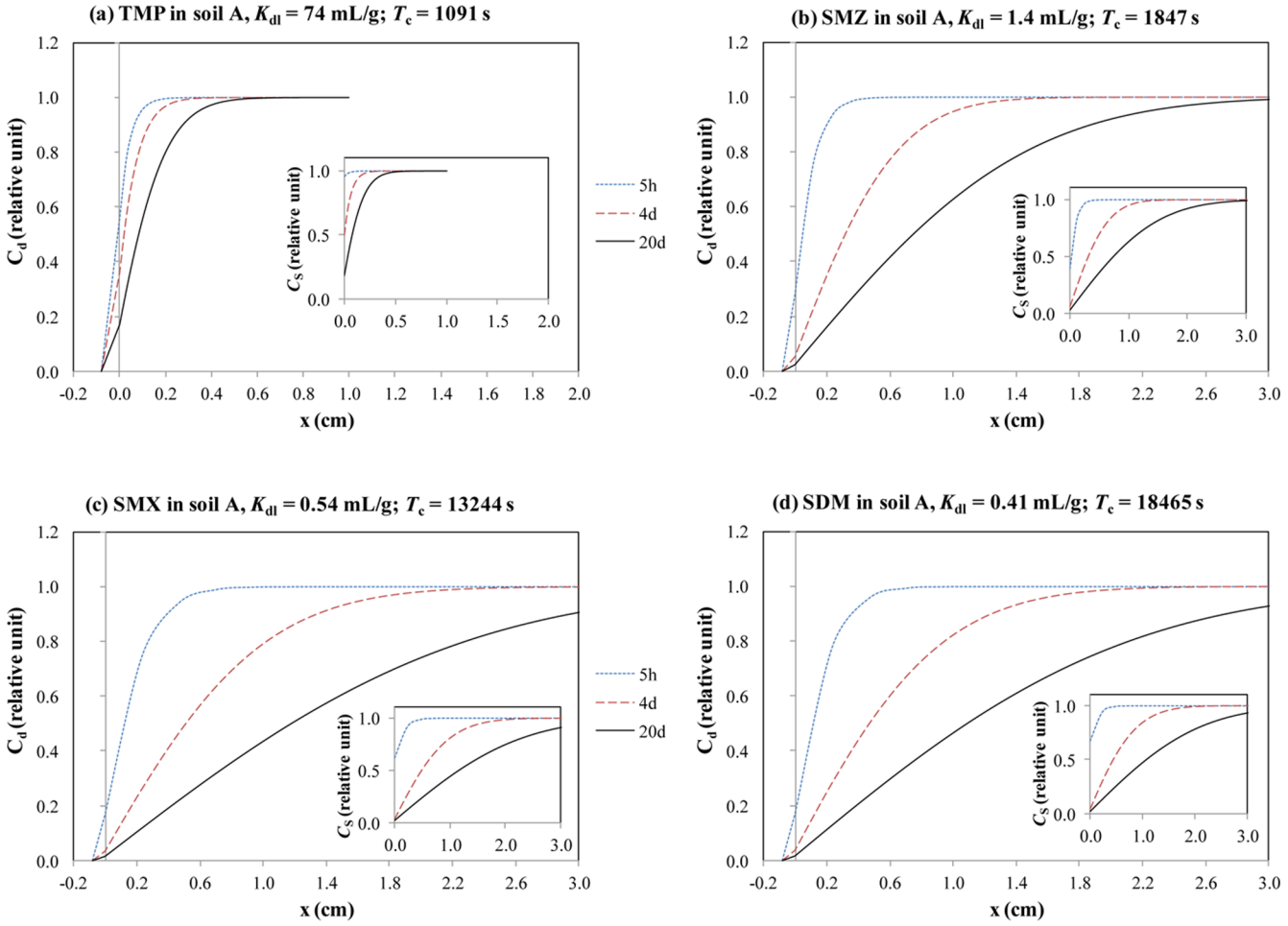


Figure 4. DIFS model (1D) output for four antibiotics in soil A simulating the dependence of C_d and C_s (inset figures) on distance from the DGT interface at a deployment time of 5 h (dotted line), 4 d (dashed line), and 20 d (continuous line). The best fit values of K_{dl} and T_c were used for each antibiotic and soil (from Figure 3).

of these antibiotics in the system at the beginning (5 h), middle (4 d), and end (20 d) of this study are given in Figure 4 for soil A and Figure S1 in Supporting Information for soil B. They are normalized to the maximum concentration in either solution, C_d, or solid phase, C_s. For TMP in soil B, where T_c is relatively small (faster resupply), the C_d profile reflects the profile shape of C_s quite well at any time during the deployment (Figure S1a). When there is effective equilibration between solid phase and solution (rapid exchange kinetics), the proportional decline in solution and solid phase concentrations are equal. However, for soil A (with a similar K_{dl}) where T_c was higher, the decline of C_d was more pronounced than the depletion of C_s (Figure 4a) at short times (e.g., 5 h), but not for longer times (>4 d). This indicated that there is kinetic limitation at short deployment time, but not at longer deployment times. The depletions of the C_d and C_s for TMP in both soils never extend very far away from the filter (<0.6 cm). In contrast, the smaller values of K_{dl} and larger values of T_c for SAs in both soils results in the depletions of C_d and C_s extending further into the soil. The decline of C_d was more pronounced than the depletion of C_s, but only at short times (e.g., 5 h) (Figure 4b,c,d and Figure S1b,c,d). Therefore, K_{dl} controls the ultimate resupply of these antibiotics by the soils at longer times, while T_c controls the resupply for short times for SAs in both soils and TMP in soil A.

Environmental Implications. It appears that the kinetics of release from solid phase to solution can under some circumstances control the rate of supply of antibiotics to an o-DGT device. The constraint would also apply to the uptake of antibiotics by biota, if there is rapid assimilation of antibiotics. DGT measurements of metals in soils have been shown to correlate well with their concentrations in biota,[29−31] and this has been shown to be due to the DGT device mimicking the limits of supply experienced by the biota.[32] The kinetic limitations observed in this work imply that the supply of polar organic chemicals to biota (e.g., plants) may be similarly limiting if uptake by biota is fast. Further work is underway to investigate whether o-DGT measurements of polar organic chemicals such as antibiotics might also be related to the availability of antibiotics to biota.

■ ASSOCIATED CONTENT

Supporting Information

Supplementary tables and figures as described in the text. 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.

■ ACKNOWLEDGMENTS

The authors thank Mr. Wei Chen and Dr. Suhong Pan for their kind help in the lab. We are grateful to the Chinese Scholarship Council (CSC) for sponsorship of C.-E.C. K.C.J. is grateful to the Chinese Academy of Sciences (CAS) for a Senior Visiting International Scientist Professorship position. This study was also supported by the UK-China Bridge Project.

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